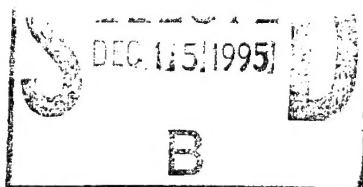


PHOTODEGRADATION AND  
BIODEGRADATION OF SOME  
POLYMERS CONTAINING CARBONYL  
GROUPS.



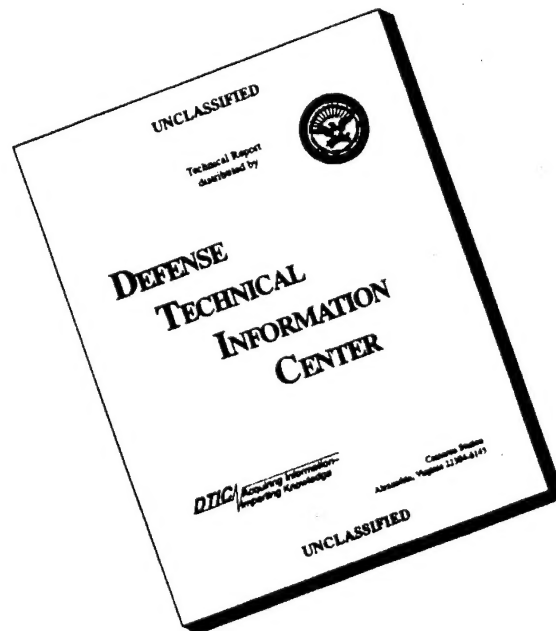
BYRNE, CATHERINE ANNE  
DEGRLE DATE: 1978

DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution Unlimited

19951214 122

# DISCLAIMER NOTICE



**THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.**

C

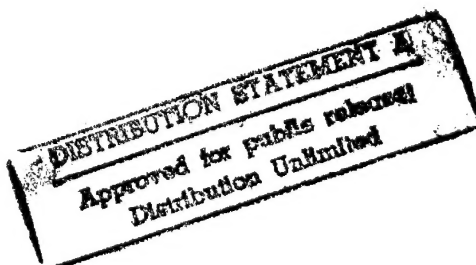
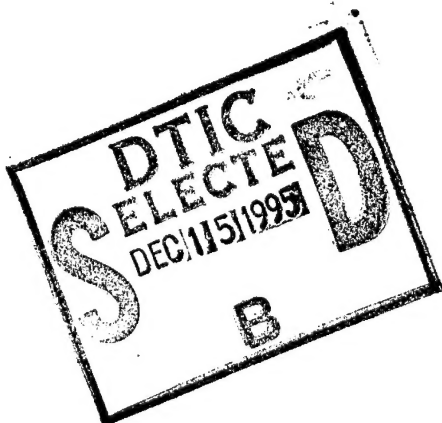
\*MSG DIA DROLS PROCESSING - LAST INPUT IGNORED

-- 1 OF 1  
--  
-- \*\*DTIC DOES NOT HAVE THIS ITEM\*\*  
-- 1 - AD NUMBER: D430949  
-- 6 - UNCLASSIFIED TITLE: PHOTOGRAPHY AND BIODEGRADATION OF SOME  
-- POLYMERS CONTAINING CARBONYL GROUPS,  
-- 10 - PERSONAL AUTHORS: BYRNE, C. A.;  
-- 11 - REPORT DATE: , 1978  
-- 12 - PAGINATION: 153P  
-- 20 - REPORT CLASSIFICATION: UNCLASSIFIED  
-- 21 - SUPPLEMENTARY NOTE: DISSERTATION SUBMITTED TO UNIVERSITY OF  
-- CONNECTICUT IN PARTIAL FULFILLMENT OF PH.D.  
-- 22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION  
-- UNLIMITED. ~~AVAILABILITY: UNIVERSITY MICROFILMS INTERNATIONAL# 300 N.~~  
-- ~~7528 RD., ANN ARBOR MI 48104, ORDER NO. 7040004~~  
-- 33 - LIMITATION CODES: 1  
-- \*\*\*\*\*

END OF DISPLAY LIST

<<ENTER NEXT COMMAND>>

This is an authorized facsimile  
and was produced by microfilm-xerography  
in 1980 by  
UNIVERSITY MICROFILMS INTERNATIONAL  
Ann Arbor, Michigan, U.S.A.  
London, England



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
<i>Printout enclosed</i>	
By <i>DTICAF memo</i>	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
<i>A-1</i>	

### INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University  
Microfilms  
International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106  
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND

DTIC QUALITY INSPECTED 2

7913004

BYRNE, CATHERINE ANNE  
PHOTODEGRADATION AND BIODEGRADATION OF SOME  
POLYMERS CONTAINING CARBONYL GROUPS.

THE UNIVERSITY OF CONNECTICUT, PH.D., 1978

University  
Microfilms  
International 300 N. ZEEB ROAD, ANN ARBOR, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ☒.

1. Glossy photographs ☒
2. Colored illustrations \_\_\_\_\_
3. Photographs with dark background \_\_\_\_\_
4. Illustrations are poor copy \_\_\_\_\_
5. Print shows through as there is text on both sides of page \_\_\_\_\_
6. Indistinct, broken or small print on several pages ☒ throughout
7. Tightly bound copy with print lost in spine \_\_\_\_\_
8. Computer printout pages with indistinct print \_\_\_\_\_
9. Page(s) \_\_\_\_\_ lacking when material received, and not available from school or author \_\_\_\_\_
10. Page(s) \_\_\_\_\_ seem to be missing in numbering only as text follows \_\_\_\_\_
11. Poor carbon copy \_\_\_\_\_
12. Not original copy, several pages with blurred type \_\_\_\_\_
13. Appendix pages are poor copy \_\_\_\_\_
14. Original copy with light type \_\_\_\_\_
15. Curling and wrinkled pages \_\_\_\_\_
16. Other \_\_\_\_\_

PHOTODEGRADATION AND BIODEGRADATION OF SOME POLYMERS  
CONTAINING CARBONYL GROUPS

Catherine A. Byrne, Ph.D.

The University of Connecticut, 1978

The photodegradation and biodegradation of polymers prepared from 4,4'-bis(chloroacetyl)diphenyl ether, 4,4'-bis(bromoacetyl)diphenyl ether and 4,4'-bis(2-bromopropionyl)diphenyl ether were investigated. The polymers included polyamines, prepared from piperazine, 4,4'-trimethylenedipiperidine and N,N'-dimethyl-1,3-propanediamine and polyesters prepared from adipic, suberic, azelaic, sebacic and 1,10-decanedicarboxylic acids.

Photodegradation of biodegradable polysebacamides was also studied, the amine portion of the polymers including 1,2-propanediamine, 2-methyl-1,2-propanediamine, ethylenediamine, piperazine and 2-hydroxy-1,3-propanediamine.

The biodegradability of the polyamines and polyesters was studied using two fungi, *Aspergillus niger* and *Aspergillus flavus*. Polyesters from diacids of eight carbons or more were degraded by *Aspergillus niger*. Polyesters of sebacic acid were degraded by *Aspergillus flavus* and by the enzyme elastase.

The polyamines were photodegradable, but the polyesters were crosslinked by ultraviolet light. There was no difference in biodegradability before and after photolysis.

The polysebacamides were photoreactive, but those derived from piperazine and 2-hydroxy-1,3-propanediamine were crosslinked by light. Some of these polymers were more biodegradable after photolysis.

**PHOTODEGRADATION AND BIODEGRADATION OF SOME POLYMERS  
CONTAINING CARBONYL GROUPS**

**Catherine A. Byrne**

**B.A., Manhattanville College, 1970  
M.A.T., Wesleyan University, 1972**

**A Dissertation**

**Submitted in Partial Fulfillment of the  
Requirements for the Degree of  
Doctor of Philosophy**

**at**

**The University of Connecticut**

**1978**

APPROVAL PAGE

Doctor of Philosophy Dissertation

PHOTODEGRADATION AND BIODEGRADATION OF SOME POLYMERS  
CONTAINING CARBONYL GROUPS

Presented by

Catherine A. Byrne, B.A., M.A.T.

Major Adviser

S. J. Huang

Associate Adviser

J. L. Johnson

Associate Adviser

R. B. Lawrence

The University of Connecticut

1978

#### ACKNOWLEDGEMENTS

I would like to thank Dr. Samuel J. Huang for his help during all phases of my graduate career.

Drs. Robert B. Fairweather and Julian F. Johnson have also assisted me in the preparation of this thesis, as well as at other times.

I am grateful to Dr. James R. Knox for the X-ray powder patterns and advice about enzymes.

Thanks to Dr. J. A. Cameron and Chris Benedict for providing fungi for biodegradation studies.

Finally, all the people who have shared days in the lab in Beach Hall are due thanks.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS . . . . .	iii
LIST OF TABLES . . . . .	vi
LIST OF SCHEMES . . . . .	vii
LIST OF ILLUSTRATIONS . . . . .	viii
 I. INTRODUCTION . . . . .	 1
II. HISTORICAL . . . . .	3
A. Biodegradability . . . . .	3
B. Role of Microorganisms and Enzymes . . . . .	4
C. Photodegradability . . . . .	4
D. Combined Photo- and Biodegradability Studies . . . . .	7
III. RESULTS AND DISCUSSION . . . . .	8
A. Introduction . . . . .	8
B. Polysebacamides . . . . .	8
1. Polymer Synthesis . . . . .	8
2. Photolysis of Model Compounds . . . . .	10
3. Polymer Photolysis . . . . .	12
4. Combined Photo- and Biodegradability Studies . . . . .	12
C. Photo- and Biodegradability of Other Polymers . . . . .	15
D. Polyamines . . . . .	17
1. Polymer Synthesis . . . . .	17
2. Model Compound Synthesis and Photolysis . . . . .	26
3. Polymer Photolysis . . . . .	31
4. Combined Photo- and Biodegradability Studies . . . . .	35
E. Polyesters . . . . .	38
1. Polymer Synthesis . . . . .	38
2. Model Compound Synthesis and Photolysis . . . . .	44
3. Polymer Photolysis . . . . .	49
4. Combined Photo- and Biodegradability Studies . . . . .	49
5. Polymer Degradability by the Enzyme Elastase . . . . .	55
IV. EXPERIMENTAL . . . . .	59
A. General Characterization and Degradation Procedures . . . . .	59
1. End-group Titrations . . . . .	59
2. Enzyme Study Method . . . . .	60
3. Microbial Growth Study . . . . .	63
4. Photolyses . . . . .	64

TABLE OF CONTENTS (continued)

	Page
B. Synthesis . . . . .	70
1. Reagents . . . . .	71
2. General Synthetic Procedures . . . . .	72
V. REPRESENTATIVE SPECTRA . . . . .	95
VI. SUMMARY . . . . .	135
VII. BIBLIOGRAPHY . . . . .	136

# LIST OF TABLES

Table	Page
1. Polysebacamides . . . . .	9
2. Photodegradation of Polysebacamides . . . . .	13
3. Growth of <i>Aspergillus niger</i> on Polysebacamides Before and After Photolysis . . . . .	14
4. Photo- and Biodegradability of other polymers . . . . .	16
5. Polyamines from 4,4'-Bis(chloroacetyl)diphenyl ether (15).	20
6. Polyamines from 4,4'-Bis(bromoacetyl)diphenyl ether (16) .	22
7. Polyamines from 4,4'-Bis(2-bromopropionyl)diphenyl ether (17) . . . . .	23
8. Photolysis of Polyamines . . . . .	33
9. Growth of Fungi on Polyamines Before and After Photolysis . . . . .	37
10. Polyesters from 4,4'-Bis(chloroacetyl)diphenyl ether (15).	40
11. Polyesters from 4,4'-Bis(bromoacetyl)diphenyl ether (16) .	41
12. Polyesters from 4,4'-Bis(2-bromopropionyl)diphenyl ether (17) . . . . .	42
13. Photolysis of polyesters . . . . .	52
14. Growth of Fungi on Polyesters Before and After Photolysis . . . . .	54
15. Ultraviolet Absorbances of Supernatants from Enzyme Study . . . . .	57
16. Concentration of Polyester Degradation Products After Enzyme Hydrolysis . . . . .	58

# LIST OF SCHEMES

	Page
1. Morrish Reactions of Polymers Containing Carbonyl Groups .	6
2. Photoreactions of Nylon Model Compounds in Water . . . . .	11
3. Reaction to Form Polyamines . . . . .	19
4. Crosslinking of Polyamines Prepared from Primary Amines . .	24
5. Preparation of Extended Polyamine . . . . .	25
6. Preparation of Polyamine Model Compounds . . . . .	28
7. Photolysis of Polyamine Model Compounds . . . . .	29
8. Reaction to Form Polyesters . . . . .	39
9. Preparation of Extended Polyester . . . . .	45
10. Preparation of Polyester Model Compounds . . . . .	47
11. Photolysis of Polyester Model Compounds . . . . .	48

# LIST OF ILLUSTRATIONS

Figure	Page
1. X-Ray Powder Pattern for Polyamine (31). . . . .	27
2. NMR of Photolysis Products of Model Compound (37). . . . .	30
3. NMR of Photolysis Products of Model Compound (38). . . . .	32
4. Ultraviolet Spectrum of Model Compound (37) in 95% Ethanol . . . . .	34
5. Most Stable Conformation of Polyamines and Model Com- pounds from 4,4'-Bis(2-bromopropionyl)diphenyl ether . . .	36
6. DSC of Polyester (50). . . . .	43
7. X-Ray Powder Pattern for Polyester (47). . . . .	46
8. NMR of Second Fraction of Photolysis Products of Model Compound (54) . . . . .	50
9. NMR of Second Fraction of Photolysis Products of Model Compound (55) . . . . .	51
10. Ultraviolet Spectrum of Model Compound (54) in 95% Ethanol. . . . .	56
11. Titration Curve for Polyamine (22). . . . .	61
12. Ultraviolet Spectrum of Model Compound (1) in 95% Ethanol. . . . .	96
13. NMR of Polysebacamide (4). . . . .	97
14. IR of Polysebacamide (4) . . . . .	98
15. DSC of Polysebacamide (4). . . . .	99
16. NMR of Polysebacamide (6). . . . .	100
17. NMR of 4,4'-Bis(chloroacetyl)diphenyl ether (15) . . . . .	101
18. NMR of 4,4'-Bis(2-bromopropionyl)diphenyl ether (17) . . .	102
19. IR of 4,4'-Bis(bromoacetyl)diphenyl ether (16) . . . . .	103
20. IR of 4,4'-Bis(2-chloropropionyl)diphenyl ether (18) . . .	104

# LIST OF ILLUSTRATIONS (continued)

Figure	Page
21. NMR of $\alpha$ -bromo-p-methoxypropiofenone (39) . . . . .	105
22. NMR of Polyamine (25). . . . .	106
23. NMR of Polyamine (28). . . . .	107
24. NMR of Polyamine (33). . . . .	108
25. NMR of Polyamine (34). . . . .	109
26. NMR of Extended Polyamine (36) . . . . .	110
27. IR of Polyamine (20) . . . . .	111
28. IR of Polyamine (29) . . . . .	112
29. IR of Polyamine (35) . . . . .	113
30. IR of Extended Polyamine (36). . . . .	114
31. NMR of Model Compound (37) . . . . .	115
32. NMR of Model Compound (38) . . . . .	116
33. IR of Model Compound (38). . . . .	117
34. DSC of Polyamine (30). . . . .	118
35. DSC of Polyamine (35). . . . .	119
36. NMR of Polyester (43). . . . .	120
37. NMR of Polyester (44). . . . .	121
38. NMR of Polyester (48). . . . .	122
39. NMR of Polyester (50). . . . .	123
40. NMR of Polyester (52). . . . .	124
41. IR of Polyester (39) . . . . .	125
42. IR of Polyester (45) . . . . .	126
43. IR of Polyester (47) . . . . .	127
44. IR of Polyester (48) . . . . .	128
45. IR of Polyester (52) . . . . .	129

LIST OF ILLUSTRATIONS (continued)

Figure	Page
46. DSC of Polyester (46). . . . .	130
47. NMR of Model Compound (54) . . . . .	131
48. NMR of Model Compound (55) . . . . .	132
49. IR of Model Compound (54). . . . .	133
50. IR of Model Compound (55). . . . .	134

## I. INTRODUCTION

The major commercially important polymers are resistant to deterioration in the environment. This is evidenced by the fact that plastic materials can be found as roadside litter, in sanitary landfill areas and along the shores of oceans and lakes and rivers.

Several years ago, scientists became interested in the modification of polymeric materials so that they would disintegrate after they were used. This opened the door for many uses for degradable materials in agriculture, as mulch, as seed holders, as flower pots.

Environmentally, there are two major ways in which plastics can degrade. One way is disintegration under the influence of living things or their by-products. The second way is by exposure to sunlight, which photochemically breaks down the macromolecules.

The two effects can occur simultaneously and the rates of the two processes are directly related. That is, both processes in general occur more rapidly in lower molecular weight materials. Degradation in one way thus increases the rate of the other.

With this in mind, an attempt was made to learn something about both the photodegradability and the biodegradability of a number of polymers. These include:

- a.) polysebacamides derived from piperazine, ethylenediamine, 1,2-propanediamine, 2-methyl-1,2-propanediamine and 2-hydroxy-1,3-propanediamine
- b.) several other polymers whose biodegradability had been previously investigated

- c.) polymers derived from 4,4'-bis(chloroacetyl)diphenyl ether,  
its bromo analog and 4,4'-bis(2-bromopropionyl)diphenyl ether
- d.) polyesters derived from the same three monomers.

## II. HISTORICAL

### A. Biodegradability

Studies of biodegradability of polymers have included testing of biopolymers, modified biopolymers, commercially important polymers and polymers designed to be degradable.

Cellophane and amylose films are degraded by microorganisms.<sup>1</sup> A polyurethane obtained from the modification of cellulose is biodegradable.<sup>2</sup> A mixture of starch and polyethylene can be utilized by microorganisms.<sup>3</sup> Starch modified by grafting of poly(methyl acrylate) is degraded by *Aspergillus niger*.<sup>4</sup>

Of the commercially important polymers, only aliphatic polyesters and low molecular weight polyethylene are biodegradable.<sup>5</sup>

Polymers designed to be biodegradable have been synthesized from biologically important monomers, such as the  $\alpha$ -amino acids.<sup>6</sup> Polyglycolate and poly (lactic acid) have been suggested as biodegradable encapsulating materials for pesticides and herbicides.<sup>7</sup> These polymers are also used in surgical sutures which decompose in the body.<sup>8</sup> Copolymers of ethylene glycol and phosgene can be molded into biodegradable bottles.<sup>9</sup> Other synthetic polymers which are degradable include Barex 210, a polyacrylonitrile based resin,<sup>10</sup> polyenamines,<sup>11,12</sup> nylons from propanediamines,<sup>12</sup> benzylated nylons<sup>13</sup> and hydrolyzed poly (p-acetoxystyrene).<sup>14</sup>

Polymers with large numbers of aromatic rings in the backbone are generally not utilized by microorganisms, but polyesters which are extended with bis(4-isocyanatophenyl) methane, an aromatic diisocyanate,

4

are biodegradable.<sup>15,16</sup> This data is significant, because much of the work of this thesis involves degradability of aromatic polymers.

#### B. Role of Microorganisms and Enzymes

Two methods have been used in this work for testing biodegradability. One is a commonly accepted method of the American Society for Testing and Materials<sup>17</sup> using fungi and the other makes use of enzymes.<sup>18,19</sup>

Fungi cause degradation of polymers by secreting enzymes. The enzymes hydrolyze the polymer into smaller fragments which the fungi can use for food -- as a source of carbon. The fungi multiply and the multiplication is taken as a measure of the amount of degradation.

A much more expensive method for measuring polymer degradation involves the use of pure enzymes. Most hydrolytic enzymes bring about the hydrolysis of the amide bonds of peptides and proteins, but some also cleave ester bonds. These enzymes are known as esterases. It is this function of the hydrolytic enzyme elastase<sup>20</sup> which makes it useful in this study.

The factors which affect the biodegradability of polymers are many and interrelated. Among them are primary (chemical) and secondary (conformational) structure, hydrophilicity, degree of crystallinity and molecular weight.

#### C. Photodegradability

Photodegradability for the purpose of this research means that the material is capable of absorbing radiation from the sun or an artificial light source of  $\lambda > 290$  nm. Little radiation of shorter wavelength (where many organic molecules absorb) reaches the earth because

it is blocked by our atmosphere. The organic functional group which absorbs in the desired region and which is readily incorporated into polymers is the carbonyl group. The absorption results in an  $n \rightarrow \pi^*$  transition with a small extinction coefficient.

There are several mechanisms by which carbonyl functional groups react photochemically. The most common are the Norrish Type I and Norrish Type II reactions, illustrated in Scheme 1. For polymers with the carbonyl group in the main chain, the Type I cleavage can lead to a decrease in molecular weight or it can lead to crosslinking.

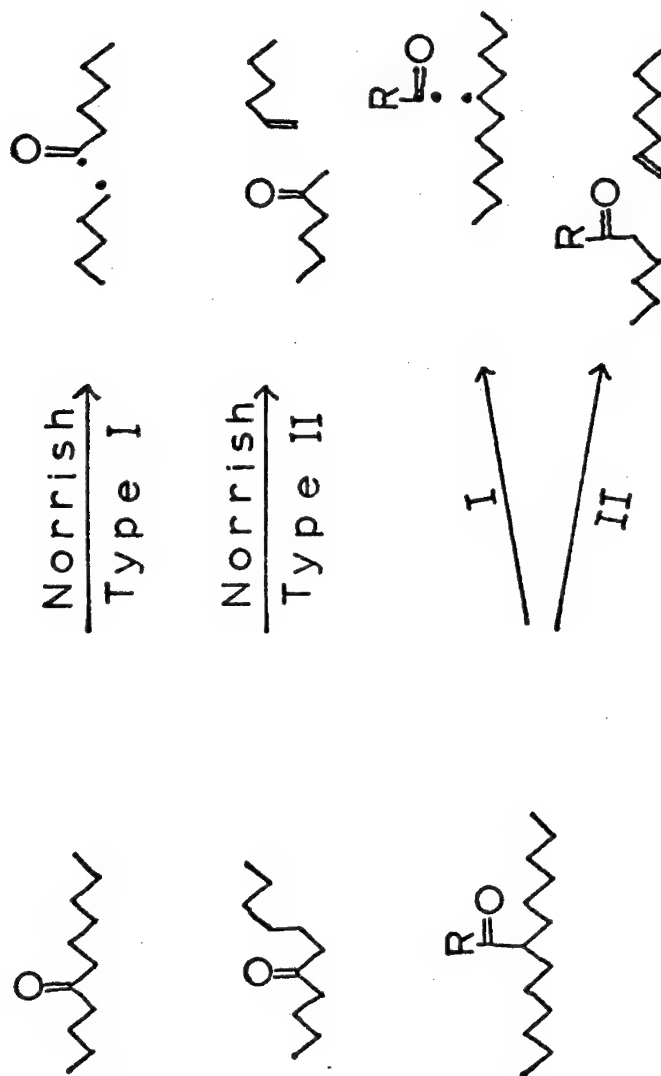
Most polymers which degrade do so via the Norrish Type II reaction, which has been called nonradical, but more probably involves a short-lived biradical.<sup>21</sup> The polymer must have a hydrogen on the carbon  $\gamma$  to the carbonyl for this reaction to occur. It proceeds through a six-membered ring transition state and leads to an olefin and a ketone end group.

Polymers with carbonyl groups directly bound to the backbone in a side chain will also degrade via a Type II mechanism. The Type I reaction does not lead to polymer cleavage in this case.

Photodegradable copolymers have been prepared from ethylene and carbon monoxide,<sup>22</sup> methyl vinyl ketone and methyl methacrylate,<sup>23</sup> methyl vinyl ketone and styrene,<sup>24</sup> and phenyl vinyl ketone and styrene.<sup>25</sup> Poly(p-methoxyacrylophenone) and its copolymers with styrene and methyl methacrylate are photodegradable.<sup>26</sup> Polyesters from diesters such as dimethyl 6-oxohendecanedioate were prepared and their photoreactivity extensively studied.<sup>21a</sup>

Scheme 1

Norrish Reactions of Polymers Containing Carbonyl Groups



D. Combined Photo- and Biodegradability Studies

There have been only a limited number of cases where both types of degradation have been combined in a single study. Bacteria and fungi isolated from soils were grown on photodegraded Ecolyte polypropylene. Ecolyte is a trademark for a specially prepared polymer containing carbonyl groups.<sup>27</sup>

Ultraviolet-sensitized samples of polystyrene, polyethylene and polypropylene were irradiated and biodegraded.<sup>28,29</sup> Irradiated polyethylene labeled with carbon-14 gave off radioactive carbon dioxide when mixed with soil rich in microorganisms.<sup>30</sup>

### III. RESULTS AND DISCUSSION

#### A. Introduction

As is apparent from the foregoing, a number of studies have been performed on the biodegradability of polymers. The same is true for investigations of photodegradability. A smaller amount of effort has been involved in attempts to combine the two forms of degradation in polymers. It is a difficult task to combine the two, because the chemical structures required for each type of degradation are generally quite different.

In this study, an attempt was made to approach the problem from two directions. Polymers which were synthesized previously for biodegradation studies were subjected to ultraviolet irradiation, to see if they might be photodegradable, even if only to a small extent.

Polymers designed to be photodegradable were synthesized and subjected to irradiation. In both cases, the biodegradability of the polymers both before and after photolysis was investigated.

#### B. Polysebacamides

##### 1. Polymer Synthesis

In this section, the photo- and biodegradability of a group of polysebacamides is reported. The series is listed in Table 1. The synthesis and biodegradability of polymers (5),<sup>12,13,31</sup> (7),<sup>12,13,32</sup> (8),<sup>33</sup> (9),<sup>12</sup> (10)<sup>12</sup> and (11)<sup>12</sup> have been extensively investigated. These polymers were originally synthesized in a study of the effects of substituents on the biodegradability of nylons. The substituents

Table 1

Polysebacamides

(3) poly(ethylene sebacamide)	$\text{+ HNCH}_2\text{CH}_2\text{NH C(=O)(CH}_2)_8\text{C(=O) +}$
(4) poly(piperazine sebacamide)	$\text{+ N } \square \text{ N C(=O)(CH}_2)_8\text{C(=O) +}$
(5) poly(methylethylene sebacamide)	$\text{+ HNCH(CH}_3\text{)CH}_2\text{NH C(=O)(CH}_2)_8\text{C(=O) +}$
(6) poly(1,1-dimethylethylene sebacamide)	$\text{+ HNC(CH}_3)_2\text{CH}_2\text{NH C(=O)(CH}_2)_8\text{C(=O) +}$
(7) poly(2-hydroxy-1,3-propylene sebacamide)	$\text{+ HNCH}_2\text{CH}_2\text{(OH)CH}_2\text{NH C(=O)(CH}_2)_8\text{C(=O) +}$
(8) poly(phenylethylene sebacamide)	$\text{+ HNCH(Ph)CH}_2\text{NH C(=O)(CH}_2)_8\text{C(=O) +}$
(9) copoly(5,75 mole %)(7,25 mole %)	
(10) copoly(5,50 mole %)(7,50 mole %)	
(11) copoly(5,25 mole %)(7,75 mole %)	

included benzyl,<sup>13</sup> phenyl,<sup>33</sup> methyl<sup>12,13</sup> and hydroxy groups.<sup>12,13</sup> Some of the benzyl, methyl and hydroxy polymers were biodegradable.

Low molecular weight amides are photochemically active,<sup>34</sup> so these polymers are appropriate samples for combined photo- and biodegradability studies. These polymers possess hydrogens  $\gamma$  to the carbonyl group both in the main chain and in side chains. Photolysis of these polymers would provide information about the ease of a Norrish Type II reaction involving either a main chain or a side chain hydrogen. If the  $\gamma$  hydrogen were in a side chain, less motion of the long polymer molecule would be required for the formation of the six-membered ring transition state through which the reaction proceeds.

Polymers (3),<sup>35,36</sup> (4)<sup>37</sup> and (6) were added in this study to make a complete series for the investigation. Poly(ethylene sebacamide) and poly(piperazine sebacamide) were synthesized interfacially, but polyamide (6) could not be synthesized in this manner.

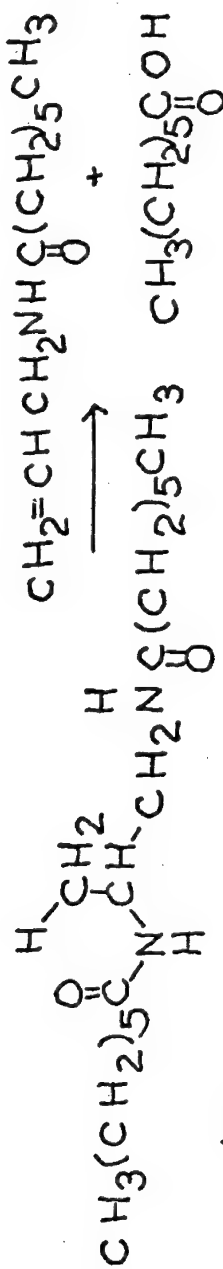
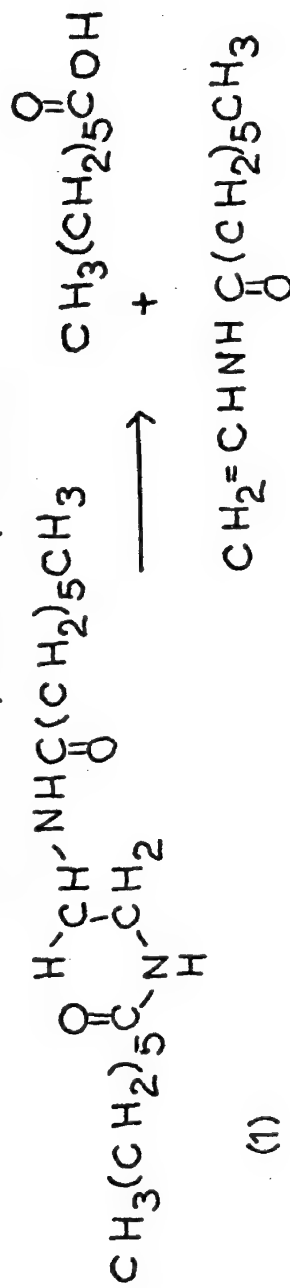
It was prepared by solution polymerization in chloroform using triethylamine as a catalyst.<sup>38</sup> The molecular weight was very low, as evidenced by  $[\eta] = 0.06$  (m-cresol, 39°C) and melting range 73-85°C.

## 2. Photolysis of Model Compounds

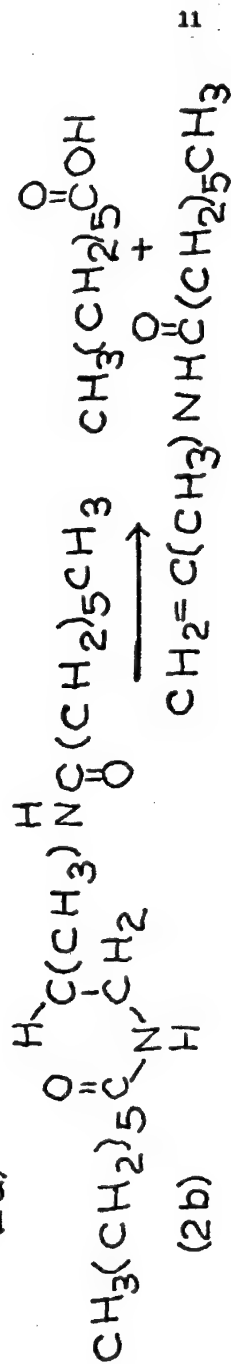
The model compounds in Scheme 2 were prepared previously for biodegradability studies.<sup>12</sup> The photolyses were carried out in aqueous suspension in air. In both cases, small amounts of the olefinic Norrish Type II product were identified by mass spectroscopy. For model (2), no information could be obtained about which isomer was formed. The other product, heptanoic acid, was not detected.

Since the photolyses were done in the presence of air, it is likely that other reactions were occurring as well, including photo-oxidation.

Scheme 2  
Photoreactions of Nylon Model Compounds in Water



(2a)



### 3. Polymer Photolysis

The polymers were photolyzed in aqueous suspension in the presence of air. The viscosities before and after photolysis were measured at 39°C in m-cresol and are shown in Table 2. Quartz was used as the light filter in most cases, because amides absorb radiation below 280 nm.

The results show that polymers (3), (5) and (6) exhibit a molecular weight decrease under the influence of ultraviolet light. Per hour of irradiation, polymer (3) degrades to a greater extent than the others. The location of a  $\gamma$  hydrogen in the side chain of polymer (5) does not make it more photoreactive than polymer (3), which has no side groups.

Polymers (4), (7) and (8) must react slowly via a Norrish Type II process, because crosslinking occurs. Steric considerations affect the reactivity of (4), which probably is not able to attain the required geometry for a Norrish Type II reaction. It is interesting to note that phenyl cyclohexyl ketone does not undergo any Type II processes.<sup>38</sup> Polymer (7) probably forms a stable free radical with an hydroxy substituent and polymer (8) a stable benzyl radical, through which crosslinking occurs.

### 4. Combined photodegradability and biodegradability studies

Polymers (0.1 g) were weighed into petri dishes and dispersed with hexane. The hexane was evaporated and half of the dishes were photolyzed through quartz for 24 hours. The samples (each in duplicate) were inoculated with *Aspergillus niger*. After four weeks the growth was recorded and is shown in Table 3.

Table 2

Photodegradation of Polysebacamides

<u>Polymer</u>	<u><math>[\eta]_{un}^a</math></u>	<u><math>[\eta]_p^b</math></u>	<u>Filter</u>	<u>Time(hr)</u>
(3)	0.36	0.24	quartz	36
(3)	0.35	0.30	pyrex	36
(4)	0.61	insoluble	quartz	24
(5)	0.57	0.51	quartz	24
(6)	0.06 <sup>c</sup>	0.05 <sup>c</sup>	quartz	24
(7)	swells	insoluble	quartz	24
(8)	-	insoluble	quartz	24

<sup>a</sup>Intrinsic viscosity of water soaked polymer before photolysis - in m-cresol at 39°C.

<sup>b</sup>Intrinsic viscosity of polymer photolyzed in aqueous suspension - in m-cresol at 39°C.

<sup>c</sup>Hexane used instead of distilled water because polymer was sticky in water.

Table 3

Growth of *Aspergillus Niger*<sup>a</sup> on Polysebacamides  
Before and After Photolysis

<u>Sample</u>	<u>Substituent</u>	<u>Before Photolysis</u>	<u>After Photolysis</u>
(1) <sup>b</sup>	none (model compound)	(0)	(0)
(2) <sup>b</sup>	CH <sub>3</sub> (model compound)	(0)	(0)
(3) <sup>c</sup>	none	(4)	(2)
(4) <sup>c</sup>	(piperazine)	(0)	(1)
(5) <sup>b</sup>	CH <sub>3</sub>	(1)	(2)
(6) <sup>c</sup>	di CH <sub>3</sub>	(1)	(2)
(7) <sup>b</sup>	OH	(3)	(4)
(9) <sup>b</sup>	CH <sub>3</sub> /OH = 3/1	(1)	(4)
(10) <sup>b</sup>	CH <sub>3</sub> /OH = 1/1	(0)	(4)
(11) <sup>b</sup>	CH <sub>3</sub> /OH = 1/3	(0)	(3)

<sup>a</sup>ASTM rating: 0 = no visible growth; 1 = < 10% surface covered; 2 = 10-30% surface covered; 3 = 30-60% surface covered; 4 = 60-100% covered.

<sup>b</sup>Passed through 60-mesh screen and weighed into petri dishes. Half the samples photolyzed.

<sup>c</sup>Photolyzed, then weighed into petri dishes and inoculated. Unphotolyzed just weighed into petri dishes and inoculated.

The results indicate that all the polymers except (3) biodegraded to a greater extent after photolysis. Since the photolyses were carried on in the presence of air, a complex mixture of reactions probably occurred. Even the polymers which crosslinked were more biodegradable after photolysis. Apparently, the increase in molecular weight by crosslinking was not as important as other factors. Perhaps some low molecular weight materials were formed, which could be utilized by the microorganisms.

The effect of photolysis on the biodegradability of the copolymers was higher than that on the homopolymers. It is quite likely that the copolymer samples were less crystalline and more susceptible to photochemical reaction in the solid state.

#### C. Photo- and Biodegradability of Other Polymers

Three other polymers whose biodegradability had been investigated earlier were also photolyzed. The results are shown in Table 4. Polymer (12)<sup>39</sup> probably crosslinked due to the formation of a stable benzyl radical. Polymer (13)<sup>19</sup> probably crosslinked due to the formation of a stable free radical with an hydroxy substituent. Only (13) was more biodegradable after photolysis. The conditions used for the tests were the same as for polyamide (4). Polymer (14),<sup>12</sup> a polymer with a methyl group as a side chain, was photodegraded to a lesser extent than poly(ethylene sebacamide), but to a greater extent than poly(methylethylene sebacamide).

### Photo- and Biodegradability of Other Polymers

Polymer	Photo		Bio.d.e	
	Before	After	Before	After
(12) $\text{HNCH}(\text{CH}_2\text{Ph})\text{C}(=\text{O})\text{OCH}_2\text{CH}_2\text{OCNH}(\text{CH}_2)_6\text{NH}\text{C}(=\text{O})^a$	$[\eta]_{\text{un}}$	$[\eta]_p$		
(13) $\text{O}(\text{CH}_2)_{12}\text{OCCH}(\text{OH})\text{CH}(\text{OH})\text{C}(=\text{O})^b$	-	crosslinked	(0-1)	(0-1)
(14) $\text{HNCH}(\text{CH}_3)\text{CH}_2\text{NH}\text{C}(=\text{O})\text{NH}(\text{CH}_2)_6\text{NH}\text{C}(=\text{O})$	1.00 <sup>c</sup>	0.80 <sup>c</sup>	(0)	(0)

<sup>e</sup>Polymers photolyzed in aqueous suspension, passed through 60-mesh screen weighed into petri dishes and inoculated. Unphotolyzed passed through 60-mesh screen, weighed into dishes and inoculated.

#### D. Polyamines

##### 1. Polymer Synthesis

In this section, a series of polyamines were prepared. These polyamines were designed to be photodegradable, with no idea of how biodegradable they might be. Monomers containing carbonyl functional groups were synthesized. These included: 1) 4,4'-bis(chloroacetyl)diphenyl ether (15), 2) 4,4'-bis(bromoacetyl)diphenyl ether (16), and 3) 4,4'-bis(2-bromopropionyl)diphenyl ether (17). Also synthesized was 4,4'-bis(2-chloropropionyl)diphenyl ether (18), but polymers could not be obtained from this material. The synthesis<sup>40</sup> of these compounds involved a Friedel-Crafts acylation in methylene chloride at -10°C. Diphenyl ether, the appropriate acid chloride or bromide and excess aluminum chloride were used. The products were ivory to yellow in color and were obtained in 26-65% yield purified.

Reaction of these monomers with three secondary amines, piperazine, 4,4'-trimethylenedipiperidine and N N'-dimethyl-1,3-propanediamine, produced the series of polyamines used in this study.

Similar polymers have been prepared by DiChamp, Tortai and Marechal<sup>41</sup> using 4,4'-bis(chloroacetyl)diphenyl ether and primary amines. No photochemical studies were performed on these polymers.

Investigation of the photochemistry of  $\alpha$ -phenacylamines<sup>42</sup> has shown that they react mainly through a Norrish Type II reaction. Photolysis of N-phenacylcyclohexylamine hydrochloride in aqueous methanol produced acetophenone and cyclohexanone (through hydrolysis of the imine photoproduct) in approximately 60% yield.

In this research, the polymers were prepared in several highly polar solvents at 80-90°C. The polymerization reaction is shown in

Scheme 3. Several different bases were used, including excess secondary amine, lithium carbonate and triethylamine. The syntheses are summarized in Tables 5, 6 and 7.

The bis(bromoacetyl)diphenyl ether was used because the bromide ion is known to be a better leaving group than chloride in a nucleophilic displacement reaction. It was thought that a higher molecular weight polymer would result, but it did not. Polymers could not be prepared from 4,4'-bis(2-chloropropionyl)diphenyl ether, presumably because the displacement reaction was too slow due to steric hindrance. Polymers were produced from the bromoanalog, but the viscosities were low and films from them were sticky and soft.

Precipitation of these polymers at the end of the reaction left the amino groups at least partially in the form of the hydrochloride. Washing with dilute ammonium hydroxide converted most, but not all of the amine hydrochloride to the free amine.

The intrinsic viscosity of polymer (29) could not be measured, because it was apparently crosslinked. Careful fractional distillation of N,N'-dimethyl-1,3-propanediamine (bp 145-6°C) did not remove traces of primary amine through which crosslinking could occur. This is illustrated in Scheme 4. Possible primary amines remaining after distillation include N-methyl-1,3-propanediamine (bp 139-141°C) and 1,3-propanediamine (bp 140°C).

Polymer (30) was extended with 1,6-diisocyanatohexane according to Scheme 5. Polyamine urea (36) was insoluble in m-cresol and trifluoroacetic acid and had  $\bar{M}_n = 1800$ .

An X-ray powder pattern was obtained for polymers (24) and (31). Samples in glass capillaries were exposed to unfiltered Cobalt K radia-

Scheme 3  
Reaction to Form Polyamines

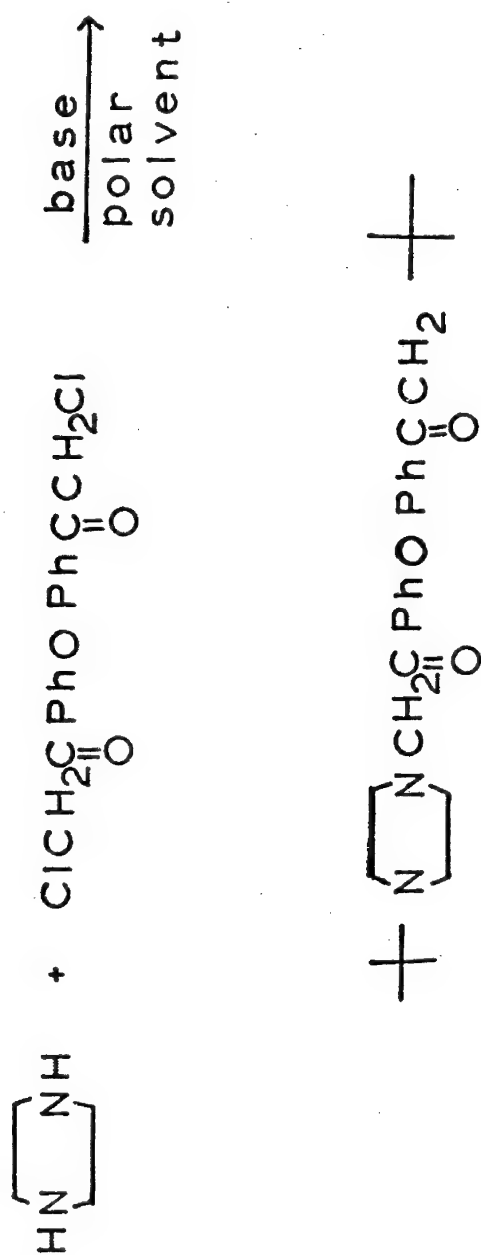
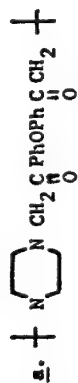


Table 5

Polyamines from 4,4'-Bis(chloroacetyl)diphenyl ether (15)



Polymer	Moles amine	Moles (15)	Moles Base	Solvent	Time(hr)	Yield (%)	$[\eta]^a$
(19)	0.02	0.01	-	HMPA	1	32	0.21
(20)	0.06	0.03	-	NMP	1	65	0.21
(21)	0.02	0.02	$\text{Li}_2\text{CO}_3$ 0.01	NMP	1	11	0.24
(22)	0.045	0.03	0.0075	NMP	1	35	0.29
(23)	0.03	0.03	0.0075	DMA	1	3	-
(24)	0.045	0.03	0.0075	NMP	3	56	0.15 <sup>b</sup>
(25)	0.009	0.006	0.003	NMP	3	61	0.14
(26)	0.0066	0.006	triethylamine 0.0132	NMP	24	83	0.22
(27)	0.009	0.006	$\text{Li}_2\text{CO}_3$ 0.0015	NMP	24	45	0.17

<sup>a</sup> Intrinsic viscosities in m-cresol at 38.4°C.<sup>b</sup> Intrinsic viscosity after formation of film from formic acid solution.

Table 5 (Continued)

$\text{b. } \left[ \text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{Ph} \right]_n$						
Polymer	Moles amine	Moles (15)	Moles Base	Solvent	Time(hr)	Yield (%)
(28)	0.06	0.03	-	HMPA	1	19
(29)	0.045	0.03	$\text{Li}_2\text{CO}_3$	NMP	3	44
$\text{c. } \left[ \text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Ph})) \right]_n$						
(30)	0.06	0.03	-	NMP	1	76
(31)	0.045	0.03	$\text{Li}_2\text{CO}_3$	NMP	3	73
						$[\eta]^a$
						0.10
						- <sup>c</sup>
						0.21 <sup>b</sup>
						0.15

<sup>a</sup> Intrinsic viscosities in m-cresol at 38.4°C.<sup>b</sup> Intrinsic viscosity after formation of film from formic acid solution.<sup>c</sup> Swelled in m-cresol.

Table 6  
 Polyamines from 4,4'-Bis(bromomethyl)diphenyl ether (16)

Polymer	Moles Amine	Moles (16)	Moles Base	Solvent	Time (hr)	Yield (%)	$[\eta]^a$
$+ \left[ \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} - \text{Ph} \end{array} \text{CH}_2 \right]_n$ (32)	0.03	0.02	$\text{Li}_2\text{CO}_3$ 0.005	NMP	24	61	0.20
$+ \left[ \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} - \text{Ph} \end{array} \text{CH}_2 \right]_n$ (33)	0.03	0.02	$\text{Li}_2\text{CO}_3$ 0.005	NMP	24	77	0.21

<sup>a</sup> Intrinsic viscosities in m-cresol at 38.4°C.

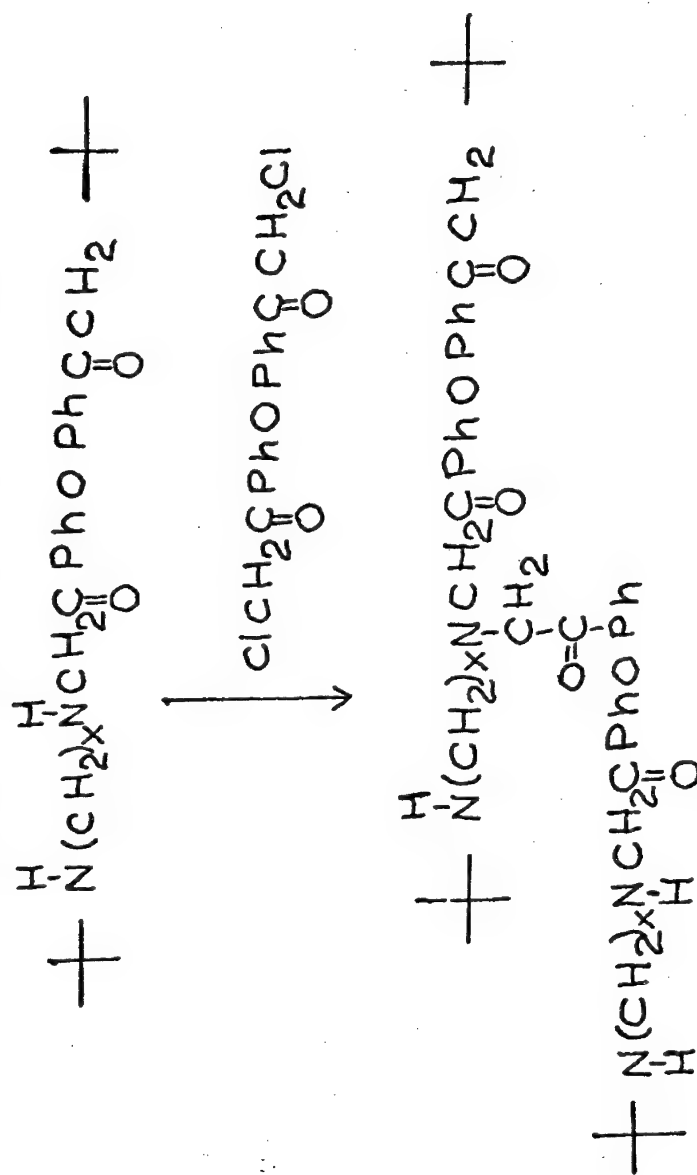
Table 7

Polyamines from 4,4'-Bis(2-bromopropionyl)diphenyl ether (17)

Polymer	Moles Amine	Moles (17)	Moles Base	Solvent	Time(hr)	Yield(%)	$[\eta]^a$
$\left[ \text{N} \begin{array}{c} \diagup \text{CH}(\text{CH}_3) \diagdown \\ \diagdown \text{CH}(\text{CH}_3) \diagup \end{array} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{CH}(\text{CH}_3) \right]_n$ (34)	0.03	0.02	$\text{Li}_2\text{CO}_3$ 0.005	NMP	24	31	0.09 <sup>b</sup>
$\left[ \text{N} \begin{array}{c} \diagup \text{CH}_2 \text{CH}_2 \diagdown \\ \diagdown \text{CH}_2 \text{CH}_2 \diagup \end{array} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{Ph} \text{O} \text{Ph} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{CH}(\text{CH}_3) \right]_n$ (35)	0.03	0.02	$\text{Li}_2\text{CO}_3$ 0.005	NMP	24	70	0.15 <sup>b</sup>

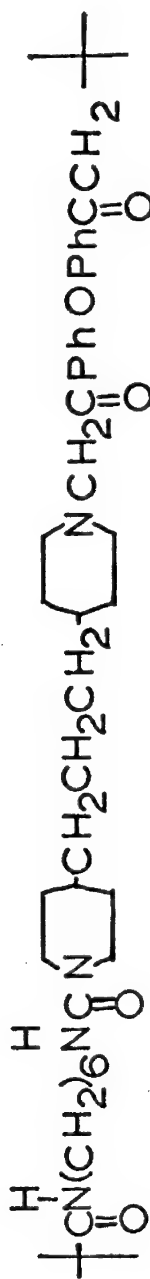
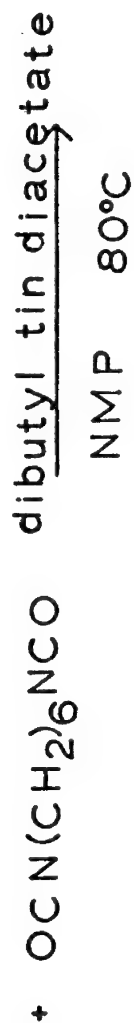
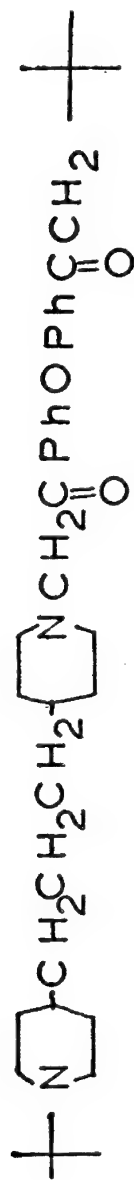
<sup>a</sup> Intrinsic viscosities at 38.4° in m-cresol.

<sup>b</sup> Intrinsic viscosity after formation of film from formic acid solution.



Scheme 5

Preparation of Extended Polyamine



tion (40 kv, 20 mA). The film-to-specimen distance was six cm and the samples were exposed for 5.9 hours at room temperature. The pattern for (31) is shown in Figure 1. It is less than 25% crystalline. Polymer (24) exhibits almost no crystallinity.

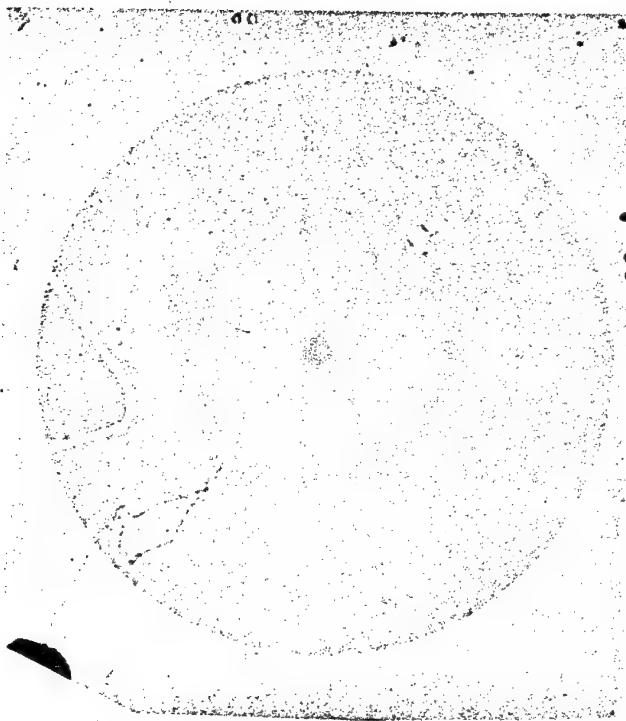
## 2. Model Compound Synthesis and Photolysis

Two model compounds were prepared for the diamine polymers. Reaction of  $\alpha$ -bromo-p-methoxyacetophenone with piperazine produced model (37) as shown in Scheme 6. In the same scheme is shown the preparation of model (38) from piperazine and  $\alpha$ -bromo-p-methoxypropionophenone (39). Starting material (39) was prepared from 2-bromopropionyl bromide, anisole and aluminum chloride in methylene chloride at  $-10^{\circ}\text{C}$ . The yield was 33%.

The model compounds were photolyzed in 1% aqueous methanol under nitrogen for 12 hours. Analysis of an NMR of the recovered solids indicated that a reaction had occurred. Separation of products by column chromatography on silica gel yielded Norrish Type II products, for model (37), p-methoxyacetophenone and for (38), p-methoxypropionophenone and mixtures of other products. The ketones were identified by high resolution mass spectroscopy. The photolysis reaction is given in Scheme 7.

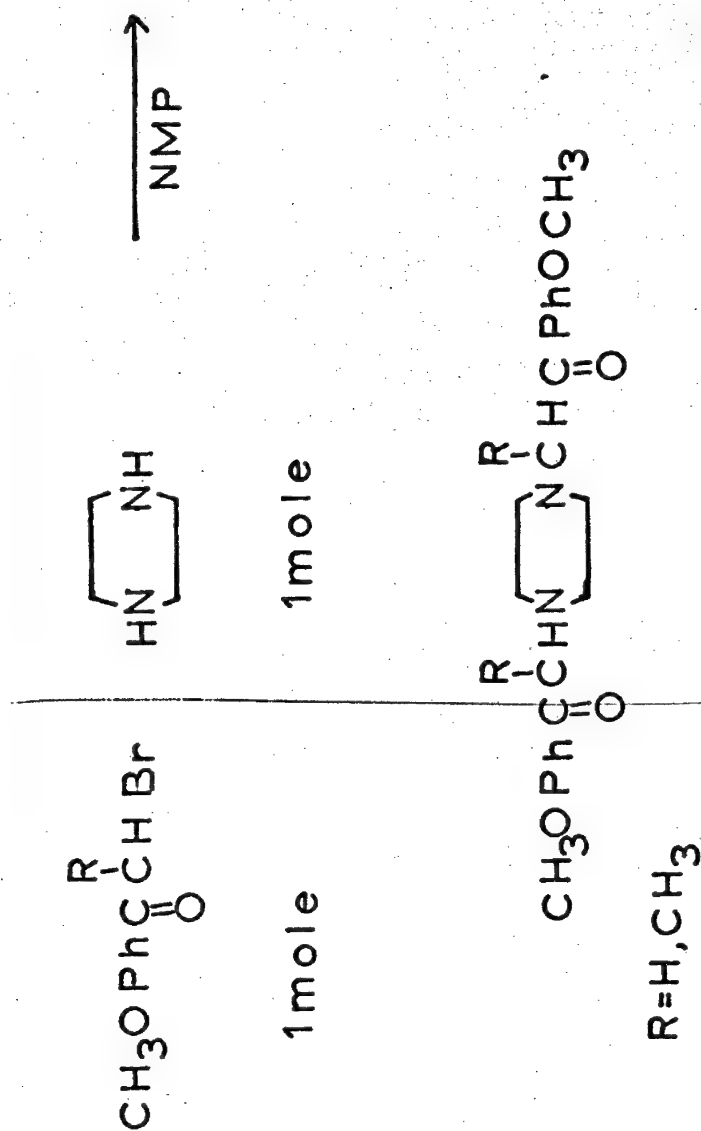
Identification of the Norrish Type II ketones<sup>42</sup> is sufficient for the purposes of this work, for it indicates that polymer chain breaking is occurring during photolysis. Analysis of the NMR in Figure 2 indicates that approximately 20% of the total possible p-methoxyacetophenone had formed. It is not very difficult to obtain this result, as the  $-\text{CH}_2-$  adjacent to nitrogen occurs at 3.75 ppm, and the  $-\text{CH}_3$  adjacent to the carbonyl occurs at 2.55 ppm.

Figure 1. X-Ray Powder Pattern for Polyamine (31).



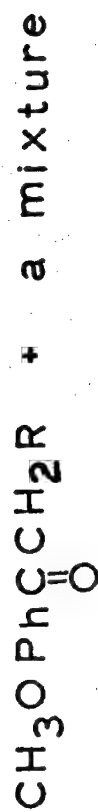
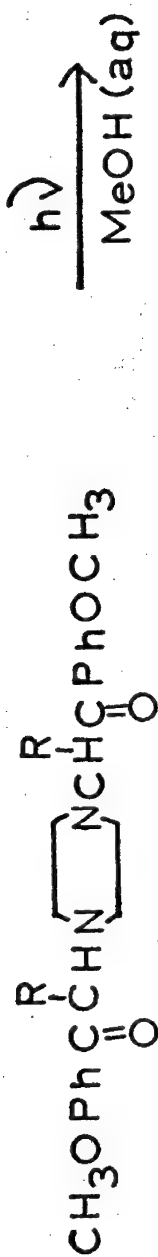
Scheme 6

Preparation of Polyamine Model Compounds



Scheme 7

Photolysis of Polyamine Model Compounds



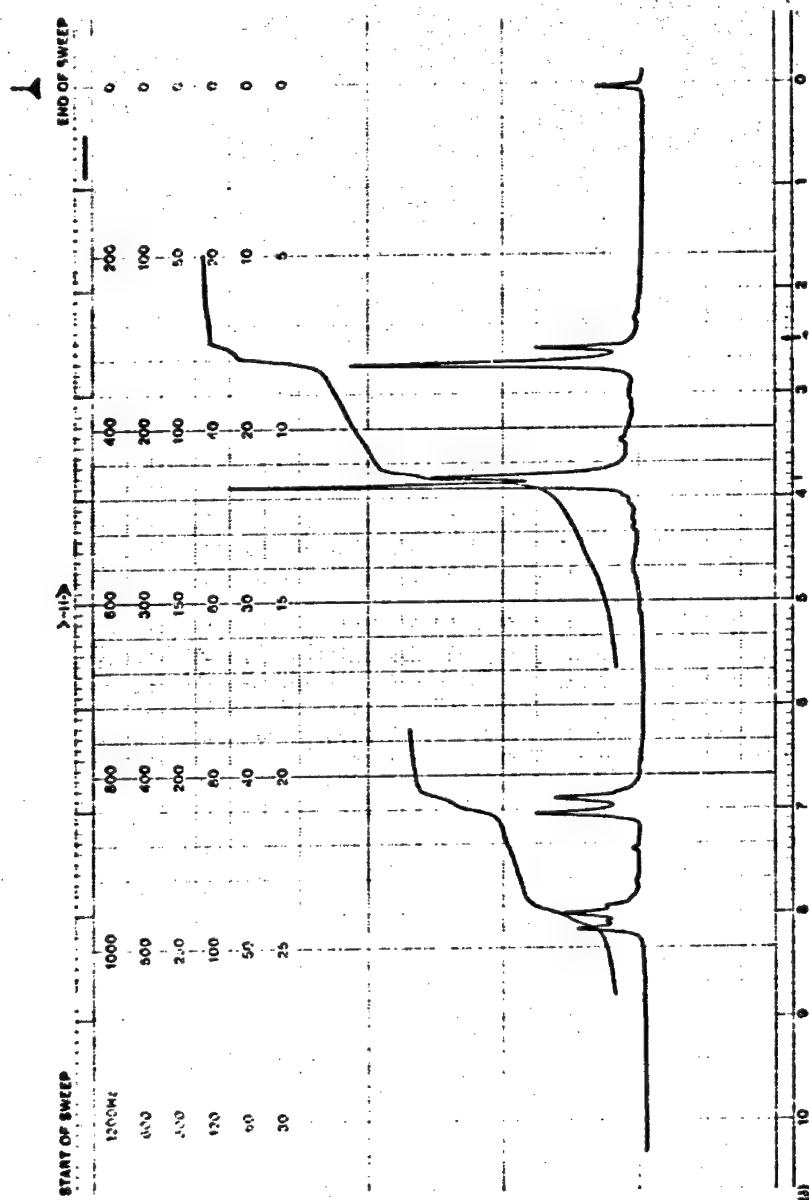


Figure 2. NMR of Photolysis Products of Model Compound (37).

In Figure 3 is the NMR for model (38). Comparison of the quartet at 4.00 ppm ( $-\text{CH}_2\text{N}-$ ) with the quartet at 2.9 ppm ( $-\text{CH}_2\text{C}-$ ) indicates that about 45% of the total possible p-methoxypropiophenone had formed. This spectrum is more difficult to interpret because the peaks overlap.

### 3. Polymer Photolysis

Representative polymers were made into films from formic acid. The carefully dried films were photolyzed in air at a uniform distance of 2.4 inches from a 450 watt Hanovia lamp. Intrinsic viscosities are shown in Table 8.

All of the polymers tested were photodegradable, but the degradation of the bis(acetyl)diphenyl ether polymers was only measurable when quartz was used as the light filter. It passes all radiation above approximately 250 nm. Pyrex passes all radiation given off by the lamp above about 300 nm. This filter more closely resembles in its emitted light the sunlight which passes to earth. The amount of degradation which occurred is related to the wavelengths of ultraviolet absorption by the polymer. The uv spectrum must be measured in solution, but no suitable solvent is available for the polymer. The uv spectra of model compounds were measured and that for model (37) is shown in Figure 4. There is no significant difference between this spectrum and that of model (38). Thus the difference in the photodegradability of the polymers must be explained in some other way.

One factor which may contribute to the greater degradability of the bis(propionyl)diphenyl ether polymers is molecular weight. Lower molecular weight compounds usually react with higher quantum yields.

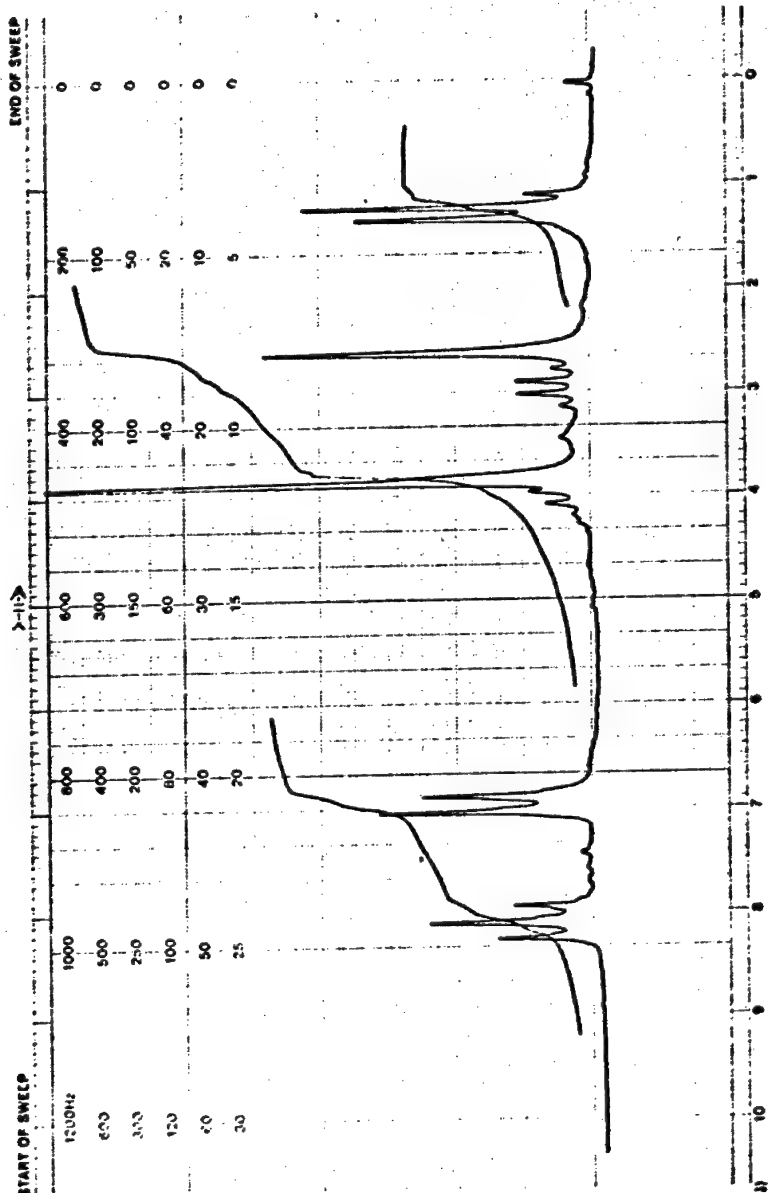


Figure 3. NMR of Photolysis Products of Model Compound (38).

Table 8

## Photolysis of Polyamines

Polymer	Filter	Time (hr)	$[n]_{un}^{a,b}$	$[n]_p^{a,c}$	Structure
(24)	pyrex 7740	24	0.15	0.15	$\left[ \text{N} \begin{array}{c} \text{CH}_2 \text{C} \text{PhO} \text{Ph} \text{C} \text{CH}_2 \\ \text{O} \end{array} \right]_n$
(26)	quartz	24	0.17	0.13	
(30)	pyrex 7740	21	0.21	0.20	$\left[ \text{N} \begin{array}{c} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{N} \text{CH}_2 \text{C} \text{PhO} \text{Ph} \text{C} \text{CH}_2 \\ \text{O} \end{array} \right]_n$
(31)	quartz	24	0.20	0.15	
(34)	pyrex 7740	24	0.09	0.06	$\left[ \text{N} \begin{array}{c} \text{CH}(\text{CH}_3) \text{C} \text{PhO} \text{Ph} \text{C} \text{CH}(\text{CH}_3) \\ \text{O} \end{array} \right]_n$
(35)	pyrex 7740	24	0.15	0.12	$\left[ \text{N} \begin{array}{c} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{NCH}(\text{CH}_3) \text{C} \text{PhO} \text{Ph} \text{C} \text{CH}(\text{CH}_3) \\ \text{O} \end{array} \right]_n$

<sup>a</sup> Intrinsic viscosities at 38.4°C in m-cresol.<sup>b</sup> Made into films from formic acid solution, ground up and dissolved in m-cresol.<sup>c</sup> Made into films from formic acid solution, photolyzed, ground up and dissolved in m-cresol.

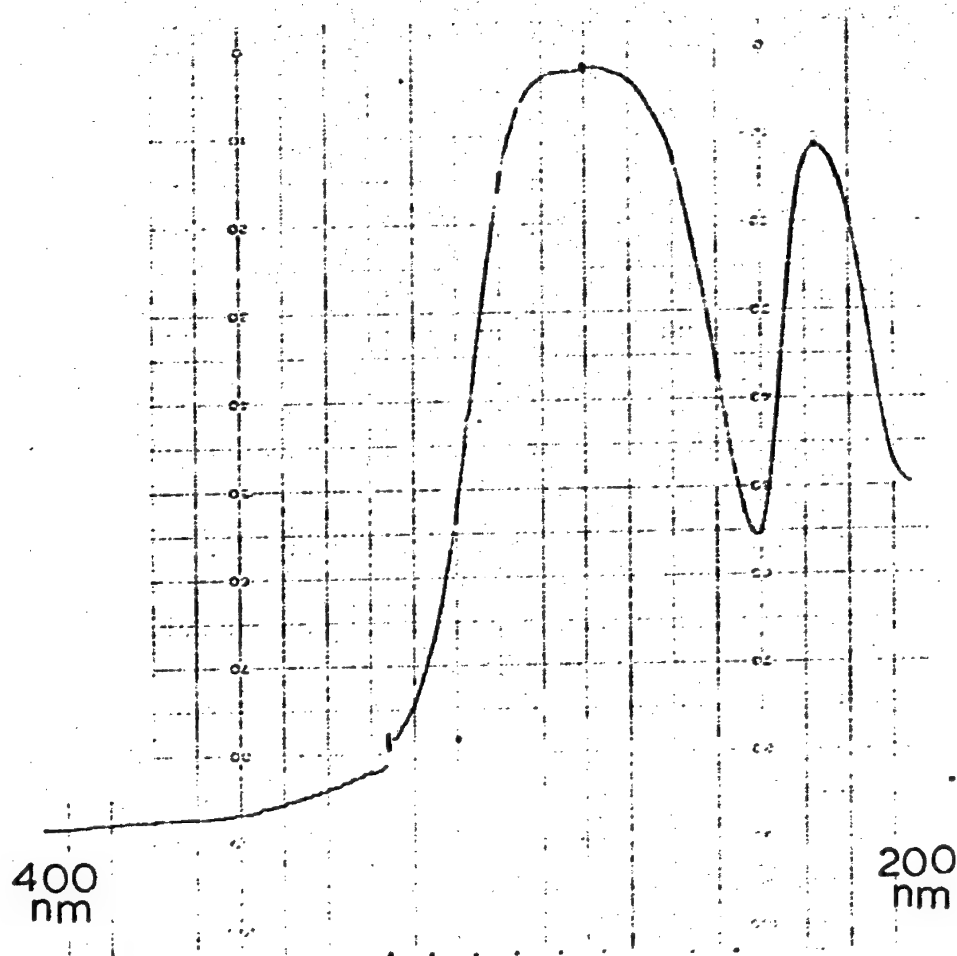


Figure 4. Ultraviolet Spectrum of Model Compound (37) in 95% Ethanol.

Since the 4,4'-bis(2-bromopropionyl)diphenyl ether was prepared from racemic 2-bromopropionyl chloride, it should consist of a mixture of enantiomers and diastereomers. Polymers prepared from this material are probably quite amorphous. Greater freedom of motion in the amorphous state increases the photoreactivity of the polymers.

Conformational analysis is also useful in explaining the difference in photodegradation. It appears that the location of the methyl group in the most stable conformation of (38) (Figure 5) allows close approach of the carbonyl group and the equatorial hydrogen  $\gamma$  to the carbonyl. No such effect occurs for model (37) and similar polymers, which can exist in other conformations of practically equal stability.

#### 4. Combined Photo- and Biodegradability Studies

Films (0.1 g) were prepared from formic acid in petri dishes and half of them were irradiated for 24 hours. Both irradiated and unirradiated samples (in duplicate) were then inoculated with *Aspergillus niger* or *Aspergillus flavus*. The results after four weeks are shown in Table 9.

Since these polymers were not utilized by either fungus, it is unlikely that enzymes would cause any degradation. Thus a study of degradation using enzymes was not done. It is not surprising that the microorganisms did not cause degradation of these polymers, since they contain no easily hydrolyzable links, such as amide or ester functional groups.

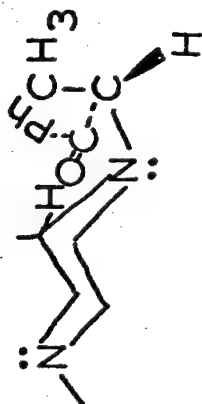


Figure 5. Most Stable Conformation of Polyamines and Model Compounds from 4,4'-Bis(2-bromopropionyl)diphenyl ether.

Table 9

Growth of Fungi on Polyamines  
Before and After Photolysis<sup>a,b</sup>

<u>Aspergillus niger</u>	<u>Before</u>	<u>After</u>
(20)	(0-1) <sup>c</sup>	(0)
(24)	(0-1)	(0)
(28)	(0)	(0)
(29)	(0)	(0)
(31)	(0)	(0)
(35)	(0-1)	(0)
(37)	(0)	(0)
 <u>Aspergillus flavus</u>		
(20)	(0)	(0)
(29)	(0)	(0)
(31)	(0)	(0)

<sup>a</sup>All samples were weighed into petri dishes and dissolved in formic acid. The acid was evaporated and half the samples were inoculated. The other half were photolyzed 24 hours through pyrex and then inoculated.

<sup>b</sup>All samples were prepared in duplicate. Values above are averages.

<sup>c</sup>ASTM rating: 0 = no visible growth; 1 = < 10% surface covered; 2 = 10-30% surface covered; 3 = 30-60% surface covered; 4 = 60-100% surface covered.

## E. Polyesters

### 1. Polymer Synthesis

In this section, a series of polyesters were prepared. Again, these polymers were designed to be photodegradable, but in this case, one might predict that as the length of the diacid portion of the polymer increases, the more likely it would be that the polymer would be biodegradable. Recall that aliphatic polyesters are the most biodegradable commercial polymers.<sup>5</sup>

Again, these polymers were prepared from 4,4'-bis(chloroacetyl)diphenyl ether (15), 4,4'-bis(bromoacetyl)diphenyl ether (16) and 4,4'-bis(2-bromopropionyl)diphenyl ether (17). Diacids of six, eight, nine, ten and twelve carbon atoms were also used. The preparation of these polymers was suggested by the work of Sheehan and Umezawa,<sup>43</sup> in which p-methoxyphenacyl and  $\alpha$ -methylphenacyl groups were used as photosensitive protecting groups for the carbonyl functions of amino acids. The photochemical reaction involves cleavage into free radicals and abstraction of hydrogen from the solvent to yield an acetophenone and the free acid.

The synthesis of these polyesters is illustrated in Scheme 8. Tables 10, 11 and 12 contain a summary of all the polymers prepared. The polymers are soluble in trifluoroacetic acid and m-cresol, but not in formic acid. They do not form films from solution. Polymers from 4,4'-bis(2-bromopropionyl)diphenyl ether were sticky and completely amorphous, as can be seen in the DSC in Figure 6, in which only decomposition exhibits an exotherm. The glass transition temperature,  $T_g$ , of these polymers must be below room temperature.

It should be noted that these polyesters, when prepared using

Scheme 8  
Reaction to Form Polyesters

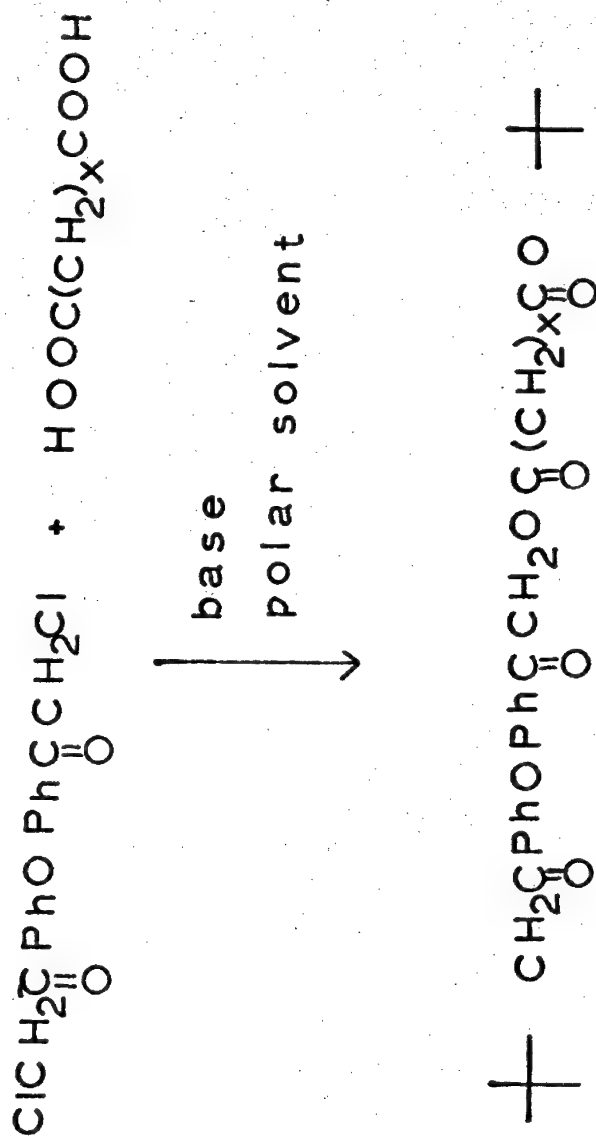


Table 10

Polyesters from 4,4'-Bis(chloroacetyl)diphenyl ether (15)

Polymer	Moles Dicid	Moles (15)	Moles Base	Solvent	Temperature (°C)	Time (hr)	Yield (%)	$[\eta]^a$
(39)	terephthalic 0.02	0.02	Et <sub>3</sub> N 0.04	DMF	0°	48	72	insoluble
(40)	adipic 0.02	0.02	0.04	DMF	0°	48	78	0.12
(41)	adipic 0.02	0.02	0.04	NMP	0°	48	84	0.20
(42)	sebacic 0.02	0.02	0.04	DMF	0°	48	80	0.15
(43)	azelaic 0.02	0.02	0.04	NMP	0°	48	90	0.21
(44)	adipic 0.02	0.02	0.044	NMP	80°	18	58	0.24
(45)	suberic 0.03	0.03	0.066	NMP	80°	18	75	0.08
(46)	sebacic 0.03	0.03	0.066	NMP	80°	18	89	0.15
(47)	1,10-decanedicarboxylic 0.03	0.03	0.066	NMP	80°	18	83	0.15
(52)	sebacic 0.011	0.01	Li <sub>2</sub> CO <sub>3</sub> 0.02	NMP	80°	24	81	0.26

<sup>a</sup> Intrinsic viscosities in m-cresol at 38.4°C.

Table 11  
Polyesters from 4,4'-Bis(bromocetyl)diphenyl (16)

Polymer	Moles Diacid	Moles (16)	Moles Triethylamine	Solvent	Temperature (°C)	Time (hr)	Yield (%)	$[\eta]^a$
(48)	sebacic 0.02	0.02	0.044	NMP	80°	18	49	0.15
(49)	1,10-decanedicarboxylic 0.02	0.02	0.044	NMP	80°	18	23	0.07

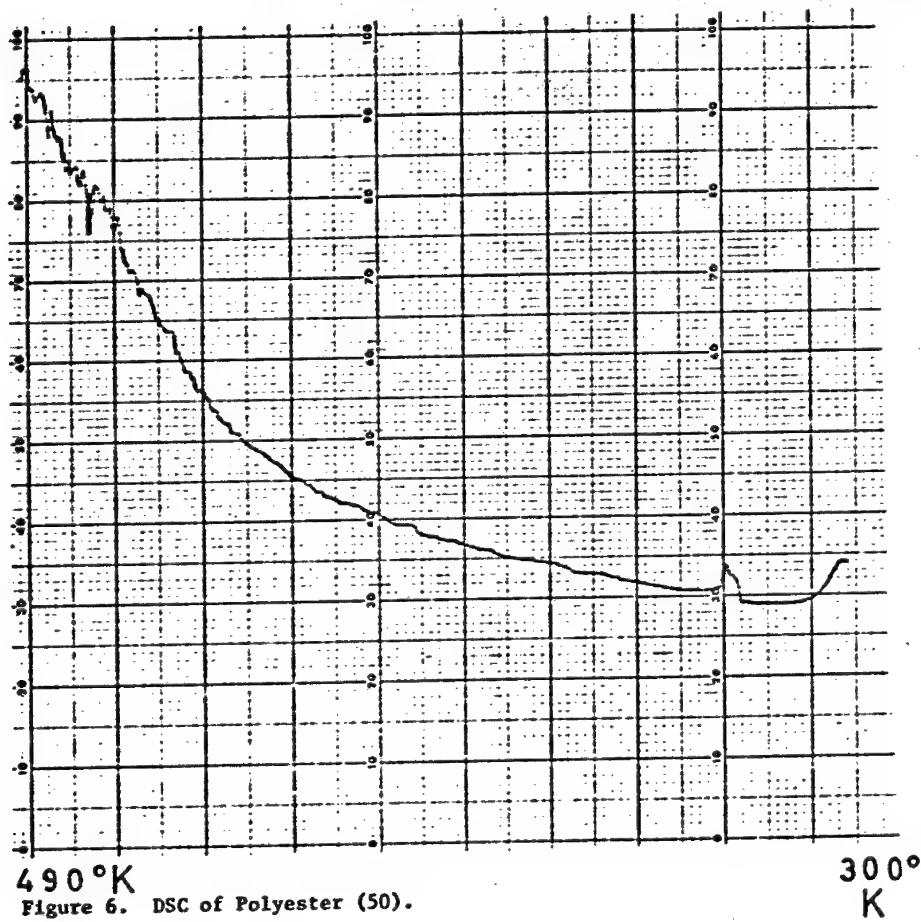
<sup>a</sup>Intrinsic viscosities at 38.4°C in m-cresol.

Table 12

Polyesters from 4,4'-Bis(2-bromopropionyl)diphenyl ether (17)

<u>Polymer</u>	<u>Moles Diacid</u>	<u>Moles (17)</u>	<u>Moles Triethylamine</u>	<u>Solvent</u>	<u>Temperature (°C)</u>	<u>Time (hr)</u>	<u>Yield (%)</u>	<u>[<math>\eta</math>]<sup>a</sup></u>
(50)	sebacic 0.02	0.02	0.044	NMP	80°	24	49	0.12
(51)	1,10-decanedicarboxylic 0.02	0.02	0.044	NMP	80°	24	14	0.13

<sup>a</sup> Intrinsic viscosities at 38.4°C in m-cresol.



triethylamine, still contained traces of the amine after purification. Washing, as well as reprecipitation with distilled water, dilute hydrochloric acid or dilute ammonium hydroxide did not remove all of the triethylamine. It is undoubtedly bound ionically to the polymer end groups -- either in the form  $(-\text{COO}^-\text{NR}_3^+\text{H})$  or  $(-\text{CH}_2\text{N}^+\text{R}_3\text{Cl}^-)$ .

Polymer (44) was extended with 1,6-diisocyanatohexane according to Scheme 9. The reaction of a carboxylic acid with an isocyanate is a complex organic reaction, in which the products depend on the concentrations of the reactive species and the catalyst.<sup>44</sup> It is impossible to obtain information from the NMR, other than that a reaction occurred. However, the intrinsic viscosity of the polymer was increased from 0.24 (44) to 0.64 (53, *m*-cresol, 38.4°C). It is most likely that polymer (53) exists as the mixed anhydride, because the acid concentration was kept low compared to the isocyanate concentration during the reaction.

X-ray powder patterns were obtained for polymers (46) and (47). The irradiation conditions were the same as those used for polyamine (31). The pattern for (47) in Figure 7 indicates that it is approximately 25% crystalline. Polymer (46) is less than 25% crystalline.

## 2. Model Compound Synthesis and Photolysis

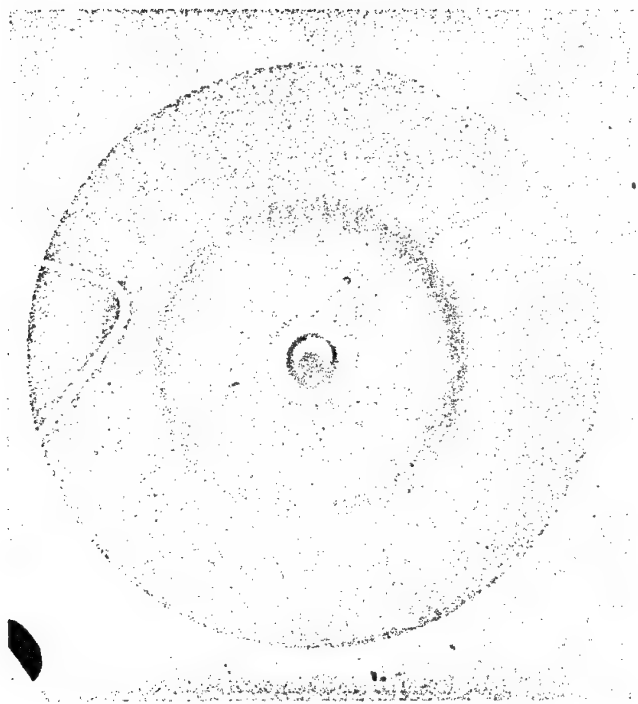
Two model compounds were prepared for the polyesters. The reaction of hexanoic acid with both 4,4'-bis(chloroacetyl)diphenyl ether (15) and 4,4'-bis(2-bromopropionyl)diphenyl ether (17) produced the model compounds, according to Scheme 10.

The model compounds were photolyzed in anhydrous ethanol for six hours, at which time no starting material remained. The photolyses reactions occurred according to Scheme 11. Acid-base extraction of the solid remaining after photolysis of (54) yielded 16% of the theoretical

## Preparation of Extended Polyester

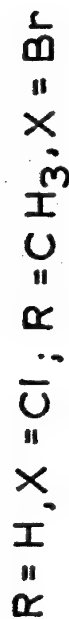
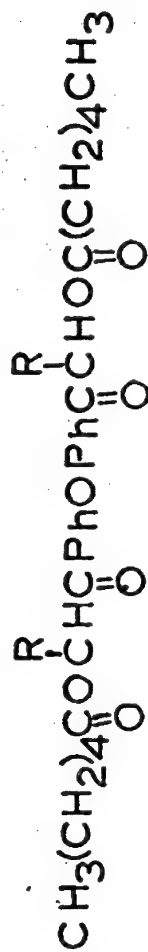
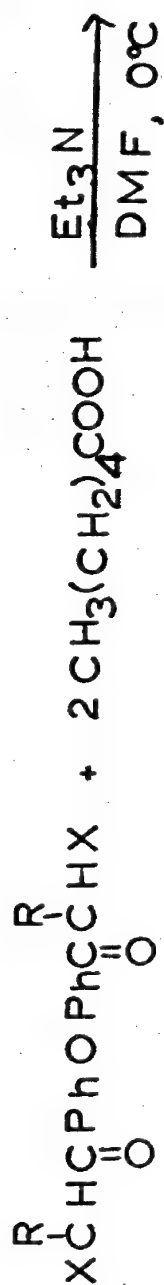


Figure 7. X-Ray Powder Pattern for Polyester (47).



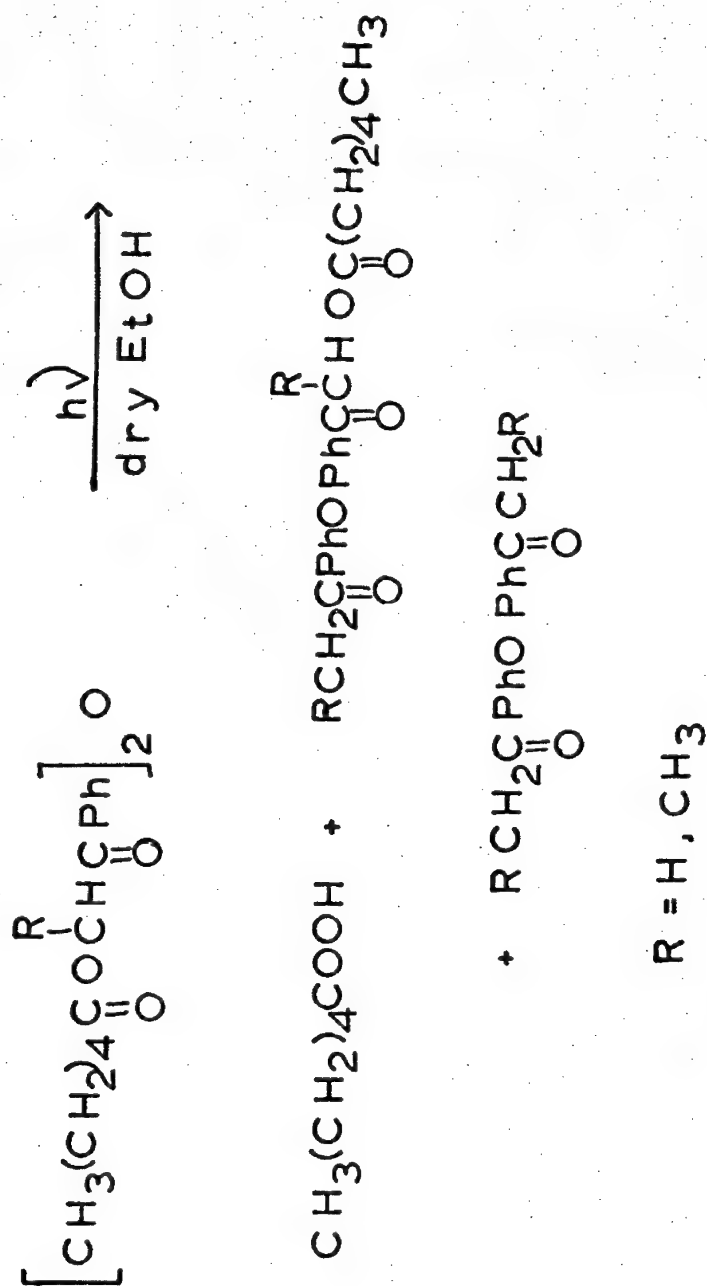
Scheme 10

Preparation of Polyester Model Compounds



Scheme 11

Photolysis of Polyester Model Compounds



amount of hexanoic acid. An attempt to purify the remaining material by column chromatography on silica gel resulted in a mixture. The NMR of this mixture is shown in Figure 8. The peak at  $\delta$  5.3 indicates that only a small amount of monoester remains. The peak at  $\delta$  2.6 indicates that the greater portion of this mixture is 4,4'-bis(acetyl)diphenyl ether. The three products were identified by high resolution mass spectroscopy.

For model (55), the yield of hexanoic acid was 32%. The NMR of the purified mixture (Figure 9) indicates that about two-thirds of the ester links have been converted to ethyl groups. The quartet at  $\delta$  6.0 is due to the methyne hydrogen and that at  $\delta$  3.0 is due to the methylene hydrogens in 4,4'-bis(propionyl)diphenyl ether. Again, the products were identified by high resolution mass spectroscopy.

### 3. Polymer Photolysis

Photolysis of representative polymers under several different conditions indicated that the polymers were not photodegradable, but photocrosslinkable. The results are shown in Table 13. Polymers prepared from 4,4'-bis(2-bromopropionyl)diphenyl ether were too sticky to photolyze.

The crosslinking reaction was faster than hydrogen abstraction from water or ethanol. This was true probably because the polymers were only suspended and not dissolved. Perhaps photolysis of the polymers in a suitable solvent, if one could be found, would yield a different result.

### 4. Combined Photo- and Biodegradability Studies

An effort was made to study the biodegradability of the polymers, both before and after photolysis. This was accomplished by

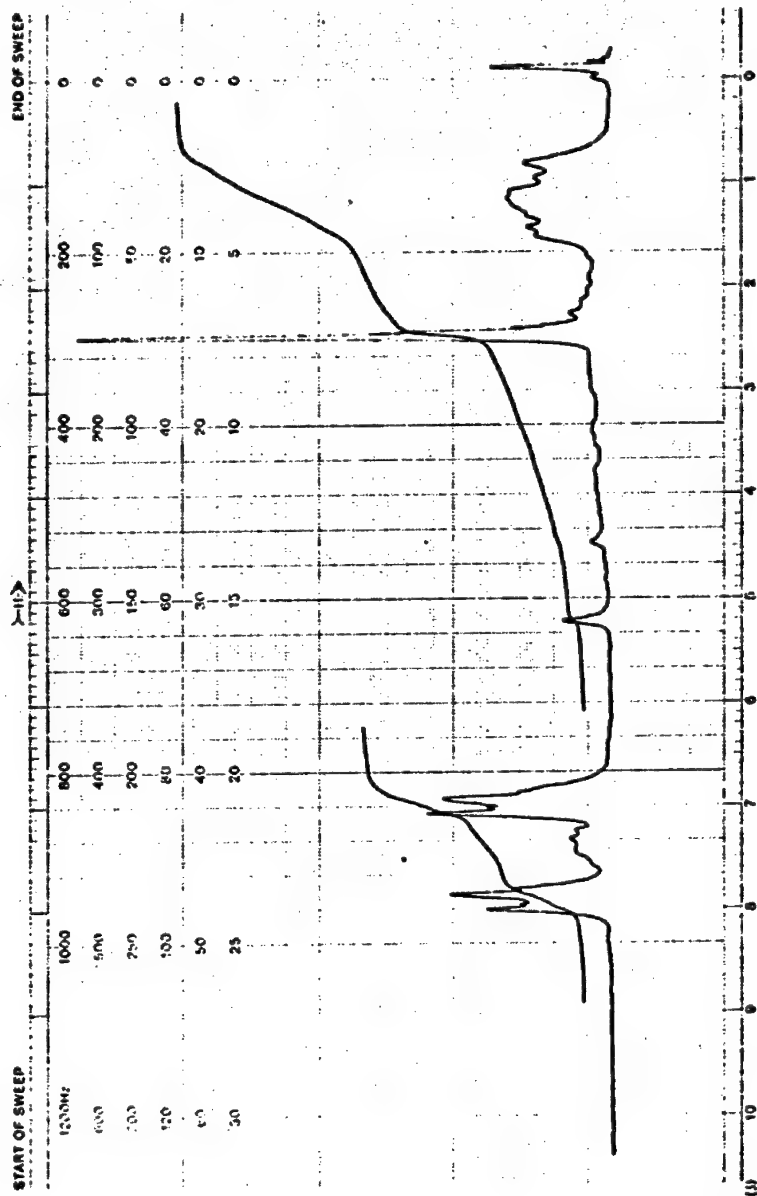


Figure 8. NMR of Second Fraction of Photolysis Products of Model Compound (54).

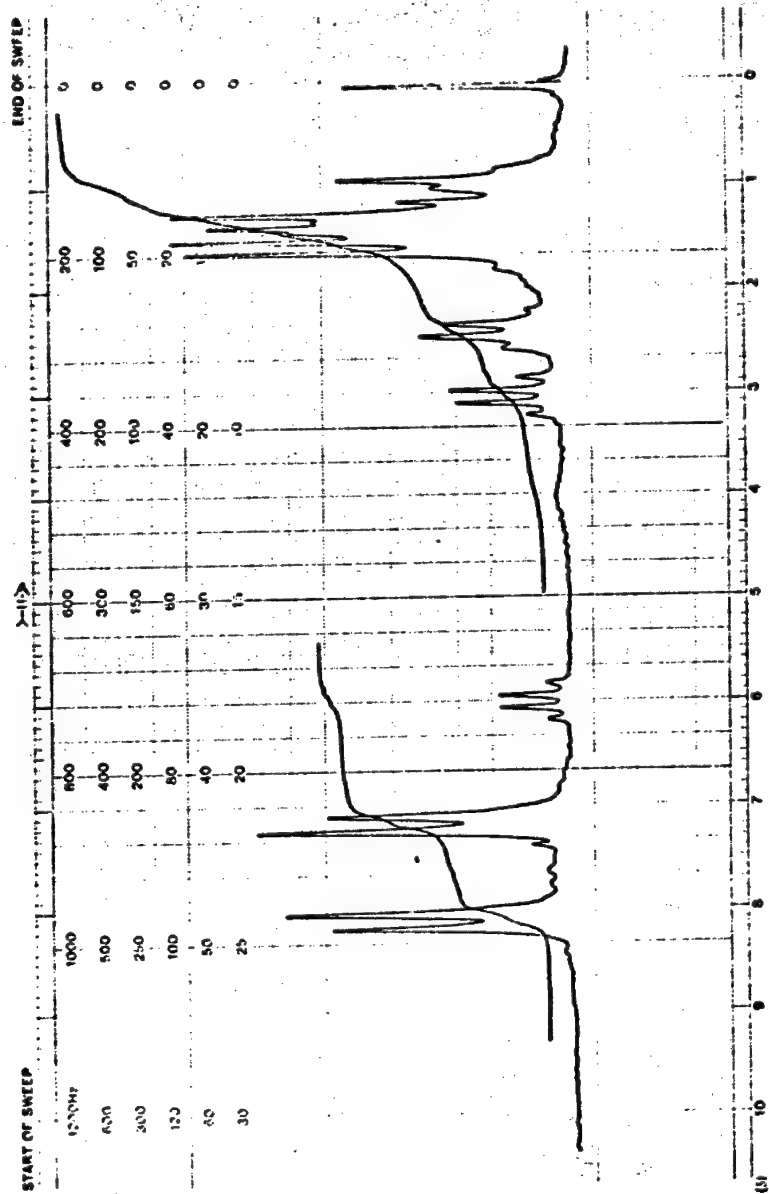


Figure 9. NMR of Second Fraction of Photolysis Products of Model Compound (55).

Table 13  
Photolysis of Polyesters

<u>Polymer</u>	<u>Filter</u>	<u>Dispersing Medium</u>	<u>[<math>\eta</math>]<sup>a</sup></u>
(46)		(stirred in H <sub>2</sub> O)	0.15 <sup>b</sup>
(46)		(stirred in EtOH)	0.14 <sup>c</sup>
(46)	pyrex 7740	H <sub>2</sub> O/air	0.16
(46)	pyrex 7740	H <sub>2</sub> O/N <sub>2</sub>	0.19
(46)	pyrex 7740	EtOH/N <sub>2</sub>	0.17
(47)	quartz	EtOH/N <sub>2</sub>	insoluble

<sup>a</sup>Intrinsic viscosities in m-cresol at 38.4°C.

<sup>b</sup>Stirred in water 24 hours, filtered, dried and dissolved in m-cresol. Some treatment as photolyzed polymers, except for irradiation.

<sup>c</sup>Same as above, except the dispersing medium was ethanol.

weighing 0.1 g of each polymer into petri dishes, dissolving in tri-fluoroacetic acid and evaporating the solvent to leave an even coating. These petri dishes were suspended around the Hanovia lamp at a uniform distance of 2.4 inches and irradiated through pyrex 7740 for 24 hours. The results of the biodegradation tests with *Aspergillus niger* and *Aspergillus flavus* are shown in Table 14.

The fact that these polymers are degradable is noteworthy, because polymers containing large numbers of aromatic rings in the backbone are commonly considered unlikely to biodegrade.

The results show very little difference in degradation before and after photolysis. The polymers with the highest biodegradability (47) and (48), are also polymers with the highest number of carbon atoms in the acid portion of the polymer chains. This was predicted, because these polymers more closely resemble aliphatic polyesters in structure.

The data also indicate that the growth of the fungus is related to molecular weight. Polymers (46), (48) and (52) were all prepared from sebacic acid, but the biodegradability increases in the order (52) < (46) < (48). Polymer (52) has an intrinsic viscosity of 0.26, as compared with 0.15 for both (46) and (48). Other factors must also be considered, including degree of crystallinity and presence of trace amounts of catalyst.

It is interesting that the polymers from 4,4'-bis(2-bromopropionyl)diphenyl ether (17), (50) and (51), are not very degradable, even though they contain sebacic acid and 1,10-decanedicarboxylic acid. Possibly steric hindrance to the site of hydrolysis, the ester bond, is provided by the methyl group.

Table 14

Growth of Fungi on Polyesters Before and After Photolysis<sup>a,b,c</sup>

Aspergillus niger

<u>Polymer</u>	<u>Number of Carbon Atoms in Diacid</u>	<u>Before</u>	<u>After</u>
(40)	6	(0-1)	(0)
(42)	10	(1)	(0-1)
(43)	9	(1)	(1)
(44)	6	(0)	(0-1)
(45)	8	(1-2)	(1-2)
(46)	10	(1-2)	(1-2)
(47)	12	(2-3)	(2-3)
(48)	10	(2-3)	(2-3)
(50)	10	(0)	(1)
(51)	12	(0)	(1)
(52)	10	(1)	(0)
(54)	(model compound)	(0)	(0) <sup>d</sup>

Aspergillus flavus

(44)	6	(0)	-
(46)	10	(0)	-
(47)	12	(0)	-
(48)	10	(2)	-
(52)	10	(0)	-
(54)	-	(0) <sup>d</sup>	-

<sup>a</sup> ASTM rating: 0 = no visible growth; 1 = < 10% surface growth; 2 = 10-30% surface growth; 3 = 30-60% surface growth; 4 = 60-100% surface growth.

<sup>b</sup> All samples were prepared in duplicate. Values above are averages.

<sup>c</sup> Samples were weighed into petri dishes and dissolved in trifluoroacetic acid. The acid was evaporated and half the samples were inoculated. The other half were photolyzed 24 hours through pyrex and then inoculated.

<sup>d</sup> Model compound weighed into petri dishes and photolyzed. Not dissolved in trifluoroacetic acid.

### 5. Polymer Degradability by the Enzyme Elastase

Elastase is an enzyme which has some esterase activity, and so it was used in this study of biodegradability. Polymer samples were suspended in buffer and enzyme was added daily for ten days. Then, the supernatant was analyzed by ultraviolet spectroscopy. Absorbances for model (54) in 95% ethanol at 226 nm and 277 nm were chosen as the wavelengths to be compared. The uv spectrum of model (54) is shown in Figure 10. The results (Table 15) are averages of two trials. The differences between the value for Buffer plus Polymer plus Enzyme and Buffer plus Polymer must be greater than the difference between Buffer plus Enzyme and Buffer for degradation to have occurred.

In only two cases do the absorbances indicate degradation, for polymers (48) and (50). The amount of degradation can be calculated using the extinction coefficients for model (54) at the wavelengths 226 nm and 277 nm. At 226,  $\epsilon = 11,269$  and at 277,  $\epsilon = 11,810$ . The calculations of  $\epsilon$  are shown in the experimental section. The concentrations of degradation products in solution can be calculated from the equation  $c = \frac{A\Delta}{\epsilon}$  at each wavelength. The results are shown in Table 16.

Polymer (48) is the only polymer which supported the growth of *Aspergillus flavus*, as well as supporting the highest growth of *Aspergillus niger*. This polymer was prepared from 4,4'-bis(bromoacetyl)diphenyl ether and contained more triethylamine (by NMR) than the other polymers even after repeated washing. It is also one of the lower molecular weight polymers prepared from sebacic acid.

Polymer (50) is probably degraded by elastase because it is completely amorphous. It is theorized that this increases the accessibility of the hydrolysis site to the enzyme. Note that this polymer was not utilized by *Aspergillus niger*.

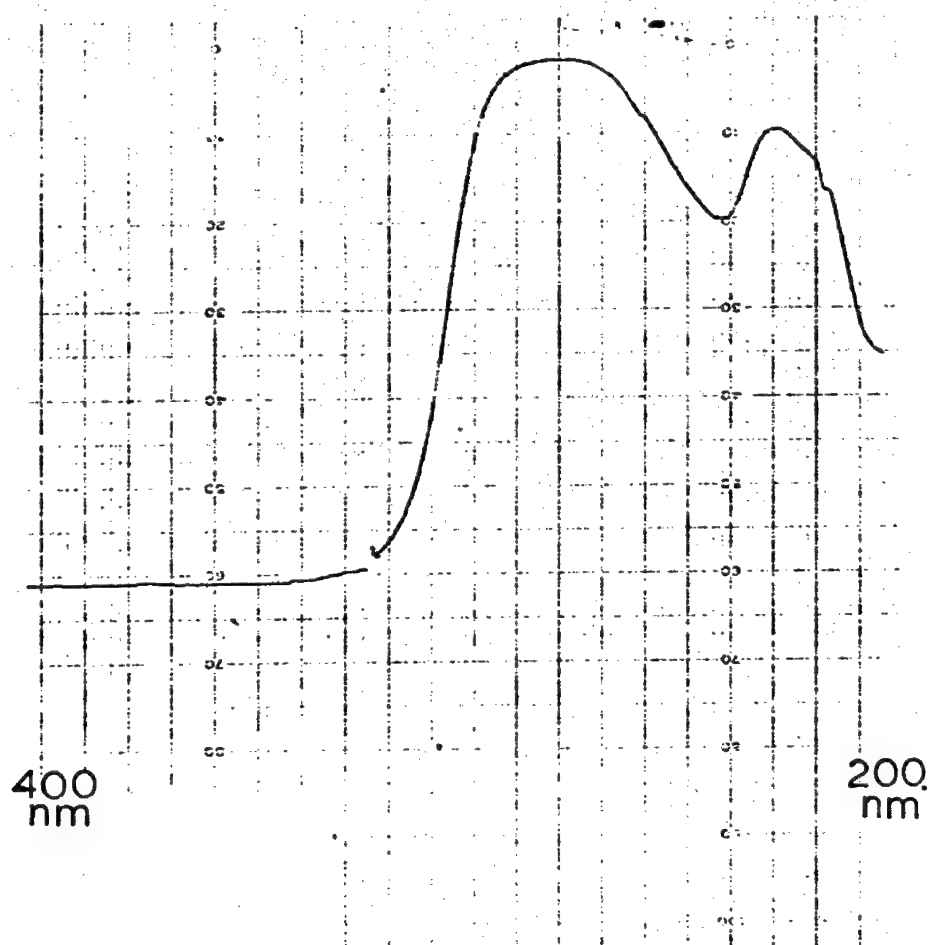


Figure 10. Ultraviolet Spectrum of Model Compound (54).

Table 13

Ultraviolet Absorbances of Supernatants From Enzyme Study<sup>a</sup>

Sample	Number of Carbon Atoms in Diacid	A <sub>277 nm</sub>	A <sub>Δ</sub>	A <sub>226 nm</sub>	A <sub>Δ</sub>
B+E		0.5074		0.5367	
B		0.5011	0.0063	0.5045	0.0322
(41) B+P+E	6	0.5092		0.5301	
(41) B+P		0.5033	0.0059	0.5068	0.0233
(43) B+P+E	9	0.5057		0.5204	
(43) B+P		0.5011	0.0046	0.5080	0.0124
(46) B+P+E	10	0.5086		0.5353	
(46) B+P		0.5011	0.0075	0.5057	0.0296
(47) B+P+E	12	0.5093		0.5318	
(47) B+P		0.5017	0.0076	0.5057	0.0261
(48) B+P+E	10	1.5281		0.9380	
(48) B+P		0.9434	0.5847	0.7686	0.1694
(50) B+P+E	10	0.5674		0.6792	
(50) B+P		0.5504	0.0170	0.5935	0.0857
(52) B+P+E	10	0.5537		0.5720	
(52) B+P		0.5568	(-0.0031)	0.5636	0.0084

<sup>a</sup>Elastase and 0.1 M Tris Buffer.

Table 16

Concentration<sup>a</sup> of Polyester Degradation Products  
After Enzyme Hydrolysis

<u>Polymer</u>	<u>Number of Carbon Atoms in Diacid</u>	<u>c<sub>277</sub> (<math>\frac{\text{mole}}{\text{liter}}</math>)</u>	<u>c<sub>226</sub> (<math>\frac{\text{mole}}{\text{liter}}</math>)</u>	<u>Average (<math>\frac{\text{mole}}{\text{liter}}</math>)</u>
(48) <sup>b</sup>	10	$4.95 \times 10^{-5}$	$1.5 \times 10^{-5}$	$3.22 \times 10^{-5}$
(50) <sup>c</sup>	10	$1.4 \times 10^{-6}$	$7.6 \times 10^{-6}$	$4.5 \times 10^{-6}$

<sup>a</sup> Calculated from equation  $c = A/\epsilon$ .

<sup>b</sup> Prepared from 4,4'-bis(bromoacetyl)diphenyl ether.

<sup>c</sup> Prepared from 4,4'-bis(2-bromopropionyl)diphenyl ether.

#### IV. EXPERIMENTAL

##### A. General Characterization and Degradation Procedures

##### 1. End-group titrations<sup>45</sup>

##### a. Polyesters

Two grams of polymer was accurately weighed into each of two 250 ml Erlenmeyer flasks. To these flasks and also to two empty flasks (blanks) were added 25 ml pyridine and a magnetic stirring bar. The flasks were heated until all the polymer dissolved at about 100°C. Ten ml distilled water was added to each and the samples were cooled.

Mixed indicator for the titration was prepared by adding one part 0.1% aqueous cresol red to three parts 0.1% aqueous thymol blue, both indicators having been neutralized with NaOH. Six drops of this solution and 10 ml n-butanol were added to each flask. The samples were titrated with 0.4 N methanolic NaOH.

The number of end groups per gram can be calculated by the formula shown below:

$$\text{Mole of end group/gram} = \frac{\text{equiv. HCl}}{1000 \text{ (ml)}} \times \frac{\text{amount of titrant (ml)}}{\text{gram of polymer}}$$

Since the number-average molecular weight is inversely related to the number of molecules per unit weight of sample,

$$\bar{M}_n = \frac{1}{\frac{\text{mole end group/g}}{2}} = \frac{1}{\text{mole end group/g}} \times 2.$$

No correction was made for the small number of -CH<sub>2</sub>Cl end groups remaining unreacted.

### b. Polyamines

In each of two 250 ml Erlenmeyer flasks were placed 1.5-2 g accurately weighed polymer, 35 g phenol, 15 g methanol and a magnetic stirrer. The flasks were heated to reflux in an attempt to dissolve the polymer. It did not completely dissolve. The samples were titrated using 0.2 N HCl and a pH meter from Analytical Measurements, Chatham, N.J. The end point was taken as the midpoint of the vertical portion of a plot of pH vs. ml titrant, as shown in Figure 11. These titrations were complicated by the fact that the change in slope was gradual, as opposed to the rapid slope change for simple acid-base titrations. This can be attributed in part to the fact that these polymers are polyamines and contain tertiary amino groups along the polymer chain which are potentially titrable. However, the number-average molecular weights obtained are in the expected range. In any case, the reaction of any tertiary amino groups with HCl would only cause the  $\bar{M}_n$  obtained to be lower than in actuality. Thus, the number-average molecular weights are not unjustifiably high.

$\bar{M}_n$  is calculated as for the polyesters.

### 2. Enzyme Study Method

Into each of four 20 ml corrosion resistant borosilicate vials was weighed approximately 0.13 g polymer exactly to four significant figures. To each of two vials used as controls was added 15 ml 0.1 M Tris buffer (titrated to pH 8 with HCl). To the other two were added 15 ml Tris buffer plus 0.01 ml elastase suspension each day for ten days. The elastase had been extracted from porcine pancreas and was obtained from Boehringer Mannheim, West Germany. The suspension had a concentration of 50 mg/7 ml. Duplicate vials were prepared of buffer

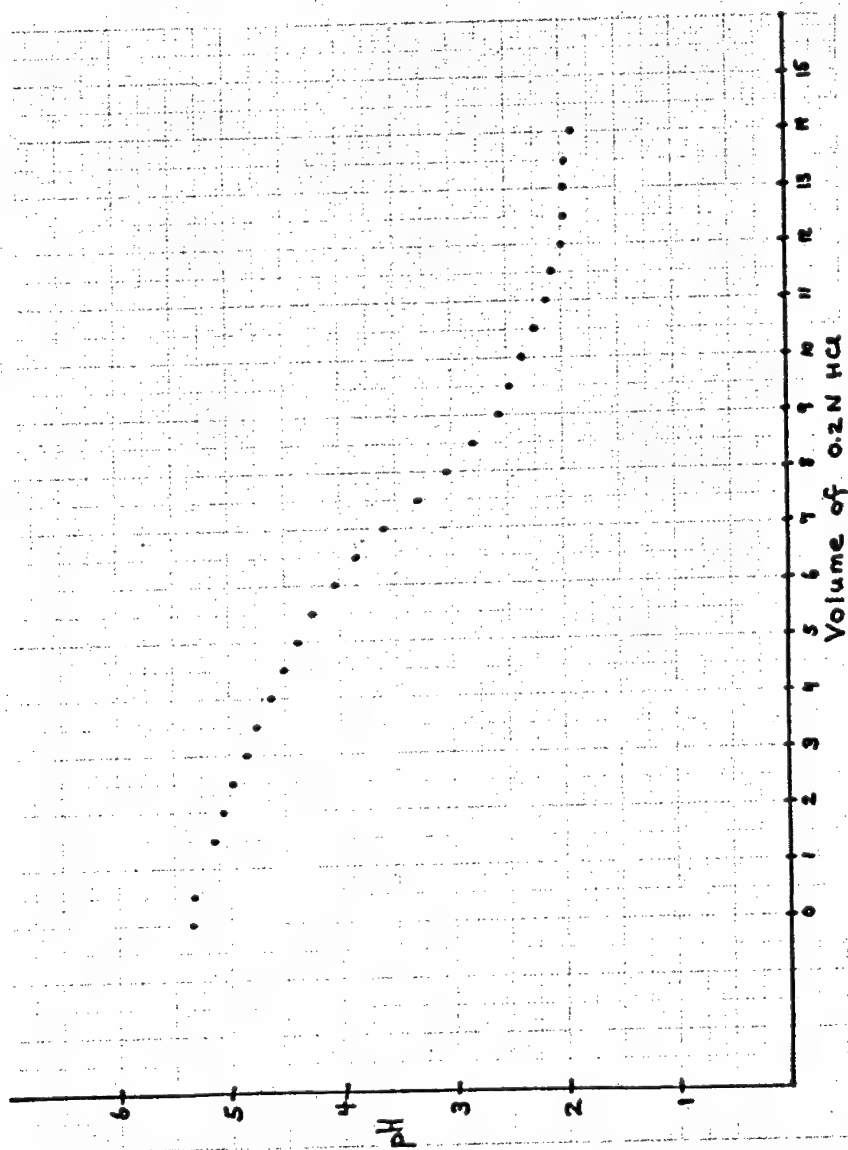


Figure 11. Titration Curve for Polyamine (22).

alone and of buffer plus enzyme. These buffer plus enzyme vials also received 0.01 ml elastase suspension each day for ten days. Vials were thoroughly shaken twice daily. At the end of the ten days, the suspensions were centrifuged and analyzed by ultraviolet analysis.

Determination of the Extent of Hydrolysis of Polyesters. Model compound (54) was dissolved in 95% ethanol to a concentration of 0.0000525 mole/l. Ethanol was used because the model was not soluble in water.

The ultraviolet spectrum of the ethanol solution showed maxima at 226 nm and at 277 nm, as can be seen in Figure 10. By the Beer's Law equation  $\epsilon = \frac{A}{c}$ , the extinction coefficients can be calculated.

For model (54), at 226 nm,

$$\epsilon = \frac{A}{c} = \frac{0.5916}{0.0000525} = 11,269.$$

At 277 nm,

$$\epsilon = \frac{A}{c} = \frac{0.6200}{0.0000525} = 11,810.$$

Absorbances for each polymer sample at those two wavelengths were calculated from the equation  $A = 1/\log T$ . Averages of duplicates were obtained.

$A_1$  = average of absorbances for buffer along

$A_2$  = average of absorbances for buffer plus enzyme

$A_3$  = average of absorbances for buffer plus polymer

$A_4$  = average of absorbances for buffer plus polymer plus enzyme.

For any degradation to have taken place,  $(A_4 - A_3) - (A_2 - A_1)$  must be greater than zero at both wavelengths. This difference is equal to the absorbance of the hydrolyzed polymer in solution. The concentration of absorbing species can be calculated from the equation  $c = \frac{A}{\epsilon}$  for each wavelength.

### 3. Microbial Growth Study

Fungi cultures were obtained from American Type Culture Collection, Rockville, Maryland. *Aspergillus niger* strain ATCC9642 and *Aspergillus flavus* strain ATCC9643 were used. Each fungus was subcultured on Sabouraud's dextrose agar or on potato dextrose agar. Subcultures were maintained at room temperature (28-30°C) for 21 days and then kept in the refrigerator at 0°C until needed.

#### Preparation of Basal Salt Solution. Stock solutions:

$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$  25 mg/250 ml distilled water

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  20 mg/100 ml

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  20 mg/100 ml

$\text{NaCl}$  25 mg/50 ml

Five ml of each of these stock solutions was added to a solution containing

0.35 g  $\text{KH}_2\text{PO}_4$

0.35 g  $\text{K}_2\text{HPO}_4$

0.35 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

0.50 g  $\text{NH}_4\text{NO}_3$

and this was made up to 500 ml in total volume. This salt solution was sterilized by placing in an oven at 120°C for at least 1 hour before using.

Preparation of Spore Suspension. The fungal spores were dislodged with a sterilized glass rod and mixed with about 30 ml sterilized basal salt solution. The mixture was filtered through sterilized glass wool into centrifuge test tubes. After centrifugation, the supernatant was discarded and 15 ml basal salt solution was added. The suspension was centrifuged again. This was repeated twice more and then the spores

were resuspended in about 50 ml basal salt solution. This suspension can be stored in the refrigerator for a maximum of four days. The concentration of *Aspergillus niger* used was  $10^6$  spores/ml. That of *Aspergillus flavus* was  $10^5$  spores/ml.

General Assay Method for Fungal Growth Study. Into 13 x 50 mm petri dishes was weighed 0.1 g of each powdered polymer. The polymers were sterilized by placing the petri dishes in a closed container saturated with formaldehyde vapor for one-half hour. One milliliter of spore suspension was added to each petri dish and the samples were incubated for four weeks in a covered container at high relative humidity and a temperature of 28-30°C.

A piece of sterilized filter paper in a petri dish was used as a viability control. The samples were prepared in duplicate and were checked once a week. At the end of four weeks, the growth on the samples was rated on a scale of 1-4. Coverage of 10% or less was rated 1; coverage of 10-30%, 2; 30-60%, 3; and 60-100% was rated 4. It is difficult in these tests to make finer distinctions with accuracy.

#### 4. Photolysis

Most of the photolyses were accomplished in a photochemical apparatus from Ace Glass Co., Vineland, New Jersey. It was equipped with a side arm mechanical stirrer, an inlet for introduction of a gas such as nitrogen, a quartz immersion well and an optional Pyrex 7740 sleeve. A 450 watt medium pressure mercury vapor lamp from Hanovia, Newark, New Jersey, was used as the light source.

A few of the samples were irradiated in a Rayonet merry-go-round photochemical apparatus from the Southern New England Ultraviolet Co., Middletown, Connecticut, using 254 nm light. The use of this equipment will be mentioned in the description of experiments.

Photolysis of model (1). In 290 ml distilled water was suspended 3.0 g bis heptanoamide of ethylenediamine. Photolysis was carried on in a photochemical reactor from Ace Glass Co. using a fused quartz immersion well and the Hanovia lamp. The reaction was allowed to proceed 24 hours in the presence of air. The recovered solid weighed 2.78 g. The aqueous filtrate was extracted with chloroform and a small amount of yellow solid remained on evaporation of the chloroform. High resolution mass spectroscopy showed an olefinic product,

$$\text{CH}_2 = \text{CH NHCO} (\text{CH}_2)_5\text{CH}_3$$

Calculated for  $\text{C}_9\text{H}_{17}\text{NO}$ : 155.1311.

Observed mass: 155.1311.

Photolysis of model (2). In 50 ml distilled water in a quartz tube was suspended 0.5 g bis heptanoamide of 1,2 propanediamine. Air was bubbled into the tube and it was photolyzed in the Rayonet for 28 hours. The model compound appeared unchanged when filtered and dried. The recovered solid weighed 0.41 g. Extraction of the aqueous filtrate with chloroform and evaporation of the chloroform yielded a small amount of solid. High resolution mass spectroscopy on the sample indicated that it contained the olefinic product,  $\text{CH}_2 = \text{CHCH}_2\text{NHCO} (\text{CH}_2)_5\text{CH}_3$  (or  $\text{CH}_3\text{CH} = \text{CH NHCO} (\text{CH}_2)_5\text{CH}_3$ ).

Calculated for  $\text{C}_{10}\text{H}_{19}\text{NO}$ : 169.1467.

Observed mass: 169.1465.

Photolysis of poly (ethylene sebacamide) (3). In 290 ml distilled water was stirred 1.5 g poly (ethylene sebacamide). The suspension was photolyzed 36 hours through quartz. The recovered solid weighed 1.48 g. A similar quantity was stirred in water for measurement of  $[\eta]_{\text{un}}$ . Viscosities were measured at 39°C in m-cresol  $[\eta]_{\text{un}} = 0.36$   $[\eta]_{\text{p}} = 0.24$ .

This polymer (1.0 g) was also photolyzed through pyrex under nitrogen for 36 hours in 290 ml distilled water. A similar quantity was also stirred in water for measurement of  $[\eta]_{un}$ .

$$[\eta]_{un} = 0.35 \quad [\eta]_p = 0.30$$

Photolysis of poly (piperazine sebacamide) (4). In 290 ml distilled water was suspended 0.75 g polyamide (4). The photolysis through quartz proceeded 24 hours. The solid recovered weighed 0.72 g. It was insoluble in m-cresol and was thus probably crosslinked by the ultra-violet light.

Photolysis of poly (methylethylene sebacamide) (5). In 290 ml distilled water was suspended 0.75 g polyamide (5). The photolysis proceeded 24 hours and the recovered solid weighed 0.66 g. A similar quantity was also stirred in water for measurement of  $[\eta]_{un}$ .

Viscosities were measured in m-cresol at 39°C.

$$[\eta]_{un} = 0.57 \quad [\eta]_p = 0.51.$$

Photolysis of poly (sebacoyl 2-methyl-1,2-propanediamide) (6). In 290 ml hexane was suspended 1.5 g polymer (6). Photolysis proceeded 24 hours. An equivalent amount of polymer was stirred in hexane 24 hours.

Viscosities were obtained in m-cresol at 39°C.

$$[\eta]_{un} = 0.06 \quad [\eta]_p = 0.05.$$

Photolysis of poly (sebacoyl 2-hydroxy-1,3-propanediamide) (7).

This polymer was photolyzed in the presence of air for 24 hours in distilled water. It turned yellow and was insoluble in m-cresol, indicating again that crosslinking had probably taken place.

Photolysis of poly (phenylethylene sebacamide) (8). In 75 ml distilled water in a quartz tube was suspended 0.5 g polymer. The

suspension was photolyzed 48 hours in the presence of air using 254 light in the Rayonet. The recovered polymer weighed 0.38 g. It appeared to be crosslinked, since it was no longer soluble in N,N-dimethylformamide or other common solvents.

Photolysis of Copoly (L-phenylalanine ethylene glycol ester-1,6-diisocyanatohexane) (12). This polymer (1.0 g) was photolyzed 24 hours in 290 ml distilled water in the presence of air. The recovered polymer weighed 0.92 g. It was insoluble in common polymer solvents and was probably crosslinked.

Photolysis of poly (dodecamethylene tartrate) (13). This polymer (0.75 g) was photolyzed 48 hours in 290 ml distilled water in the presence of air. The recovered polymer weighed 0.61 g and was insoluble in m-cresol and other common polymer solvents. The polymer was probably highly crosslinked because the unphotolyzed polymer was soluble in chloroform.

Photolysis of polyurethane (14). In 290 ml distilled water was stirred 2.0 g polymer (14). After photolysis for 24 hours in the presence of air, 1.26 g solid was recovered. A similar amount of polymer (14) was stirred in water 24 hours for use in the measurement of  $[\eta]_{un}$ .

$$[\eta]_{un} = 1.00 \quad [\eta]_p = 0.80.$$

Photolysis of model compo und (37). In 290 ml aqueous methanol (1% water) was dissolved 0.3 g model (37). Photolysis through pyrex was allowed to proceed 12 hours under nitrogen. Thin layer chromatography indicated that the reaction was not complete after 6 hours and that there was little change after 12 hours. The solvent was evaporated and the residue was dissolved in methylene chloride. Separation of components of the product mixture was attempted on a short silica gel

column using solvents of increasing polarity. In succession were added: 75 ml hexane, 75 ml 1:1 hexane/methylene chloride, 100 ml methylene chloride, 100 ml chloroform, 75 ml 2:1 chloroform/methanol, 75 ml 2:1 methanol/chloroform and 125 ml methanol. p-Methoxyacetophenone was eluted in the methylene chloride and chloroform fractions. Mixtures of products were eluted in the more polar solvents.

The p-methoxyacetophenone was submitted for analysis by mass spectroscopy.

Calculated for  $C_9H_{10}O_2$ : 150.0681.

Observed mass: 150.0680.

Photolysis of model (38). Model (38) was photolyzed and analyzed in the same way. The p-methoxypropiofenone was submitted for high resolution mass spectral analysis.

Calculated for  $C_{10}H_{12}O_2$ : 164.0837.

Observed mass: 164.0849.

Photolysis of polyamines. Each polymer (0.5 g) was dissolved in 2-3 ml formic acid on a teflon sheet. The formic acid was allowed to evaporate 3 days at 50°C at atmospheric pressure and 3 days under vacuum at 50°C. The formic acid was very tenaciously held. Films were photolyzed 24 hours, ground up and their viscosities obtained in m-cresol at 38.4°C. The viscosities of the photolyzed polymers were compared to those of polymers which had undergone the same procedure except for photolysis.

Photolysis of model compound (54). Model (54) (0.5 g) was photolyzed in dry ethanol under nitrogen six hours, at which time no starting material remained. The solvent was evaporated and the sample was redissolved in ethyl acetate. Extraction with 1 N potassium

carbonate removed the expected hexanoic acid product. Neutralization with 2 N HCl and extraction with ether yielded 0.02 g (16.67%) hexanoic acid. The ethyl acetate was evaporated and the residue was run through a short silica gel column using 4:1 chloroform/methanol to remove any polymeric products. The yield of the residue was 0.19 g [76.00%, assuming complete conversion to bis (acetyl) diphenyl ether]. The products were analyzed by high resolution mass spectroscopy.

Calculated for  $C_6H_{12}O_2$ : 116.0837.

Observed mass: 116.0831.

Calculated for  $C_{22}H_{24}O_5$  (monoester): 368.1621.

Observed: 368.1611.

Calculated for  $C_{16}H_{14}O_3$  (ether): 254.0943.

Observed mass: 254.0945.

Photolysis of model (55). This model compound (0.63 g) was photolyzed as for the previous sample. The yield after ether extraction was 0.09 g (32.14%) hexanoic acid. After purification on a short column, the residue weighed 0.24 g [70.59%, assuming complete conversion to bis (propionyl) diphenyl ether]. Samples were submitted for analysis by high resolution mass spectroscopy.

Calculated for  $C_{24}H_{28}O_5$  (monoester): 396.1936.

Observed mass: 396.1929.

Calculated for  $C_{18}H_{18}O_3$  (ether): 282.1255.

Observed mass: 282.1248.

Photolysis of Polyesters. Polyester (46) was ground up and sifted through a 60 mesh screen and used in the following experiments. The irradiation from the 450 watt Hanovia lamp was filtered through pyrex in each case.

Two grams (46) was photolyzed 24 hours in aqueous suspension in the presence of air. A similar quantity was stirred in distilled water 24 hours to be used in the measurement of  $[\eta]_{un}$ . The solid-recovered by filtration after photolysis weighed 1.89 g (94.5%) and the solid recovered after stirring in water weighed 1.85 g (92.5%). The intrinsic viscosities were measured in m-cresol at 38.4°C.

$$[\eta]_{un} = 0.15 \quad [\eta]_p = 0.16$$

Polymer (46) (1.25 g) was also photolyzed in aqueous suspension under nitrogen 24 hours. The recovered solid weighed 1.03 g (82.4%).

$$[\eta] = 0.19.$$

Photolysis of (46) (1.40 g) in anhydrous ethanol 24 hours also led to an increase in the intrinsic viscosity. The recovered solid weighed 1.19 g (85.0%). A similar quantity was stirred in dry ethanol 24 hours for measurement of  $[\eta]_{un}$ .

$$[\eta]_{un} = 0.14 \quad [\eta]_p = 0.17$$

Polyester (47) (2 g) was photolyzed through quartz in anhydrous ethanol 24 hours under nitrogen. The recovered solid weighed 4.5 g and was extensively crosslinked. It was insoluble in m-cresol and did not even swell in that solvent.

#### B. Synthesis

All melting points were uncorrected and were taken on a Reichert hot stage microscope or on a Perkin-Elmer Differential Scanning Calorimeter, DSC-1B.

Infrared spectra (ir) were recorded on a Perkin-Elmer Infracord Spectrophotometer.

Nuclear magnetic resonance spectra (nmr) were recorded on a Varian EM-360A. Solvents used include deuterated chloroform and

trifluoroacetic acid. Tetramethylsilane was used as an internal reference.

Ultraviolet spectra were recorded on a Beckman DB Spectrophotometer.

Thin layer chromatography (tlc) were performed on 0.25 mm layers of Silica Gel GF<sub>254</sub> from Merck, Darmstadt, Germany.

Elemental analyses were performed by Baron Consulting Co., Orange, Connecticut.

#### 1. Reagents

The following reagents were obtained from Aldrich Chemical Co. Inc., Milwaukee, Wisconsin: bromoacetyl bromide,  $\alpha$ -bromo-p-methoxyacetophenone, 2-bromopropionyl chloride, chloroacetyl chloride, 2-chloropropionyl chloride, m-cresol, 1,10-decanedicarboxylic acid, deuterated chloroform, 1,6-diisocyanatohexane, N,N-dimethylacetamide, N,N-dimethylformamide, diphenyl ether, hexamethylphosphoramide, 2-methyl-1,2-propanediamine, N-methylpyrrolidone, piperazine, sebacic acid, sebacoyl chloride, suberic acid, trifluoroacetic acid, and 4,4-trimethylenedipiperidine.

The following chemicals were obtained from Eastman Organic Chemicals, Rochester, New York: adipic acid, azelaic acid, 2-bromopropionyl bromide, ethylenediamine dihydrochloride and N-methylpyrrolidone.

Hexanoic acid and triethylamine were obtained from Matheson, Coleman and Bell, East Rutherford, New Jersey; dibutyl tin diacetate from Chemicals Procurement Laboratories, College Point, New York; Sabouraud's and dextrose agar from Difco, Detroit, Michigan; N,N'-dimethyl-1,3-propanediamine from Air Products and Chemicals, Allentown, Pennsylvania; anhydrous aluminum chloride from Fisher Scientific, Fair

Lawn, New Jersey; and, lithium carbonate from Mallinckrodt Chemical Works, New York.

Solvents were purified by recommended procedures<sup>46</sup> prior to use.

## 2. General Synthetic Procedures

Note: The syntheses are arranged according to procedure and not necessarily in the order in which they appear in the Results and Discussion.

Preparation of poly(ethylene sebacamide) (3).<sup>47</sup> In a quart-sized "Waring" blender were dissolved 2.66 g (0.02 mole) ethylenediamine dihydrochloride and 3.2 g (0.08 mole) sodium hydroxide in 330 ml distilled water. At low blender speed, 4.78 g (0.02 mole) sebacoyl chloride in 250 ml carbon tetrachloride was added quickly and the speed was increased to high. Blending was continued for two minutes. The white precipitate was allowed to settle overnight. It was then filtered, washed with methanol, acetone and distilled water and dried in the vacuum oven 48 hours at 50°C. The yield was 3.13 g (69.25%). ( $T_m$  = 255°C dec)  $[\eta]$  = 0.36 (m-cresol, 39°C)

ir(KBr): 3400  $\text{cm}^{-1}$  (NH); 3000  $\text{cm}^{-1}$  (OH, acid); 1700  $\text{cm}^{-1}$  (C=O, acid); 1660  $\text{cm}^{-1}$  (C=O, amide)

nmr(TFA)  $\delta$  8.6 (m, 2, NH); 3.8 (m, 4,  $\text{NCH}_2$ ); 2.67 (m, 4,  $\text{COCH}_2$ ); 1.45 (m, 12,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2$  (repeating unit): C, 63.72; H, 9.73; N, 12.39.

Found: C, 57.77; H, 8.97; N, 10.09.

Preparation of poly(piperazine sebacamide) (4). This polymer was prepared in a similar manner using 1.72 g (0.02 mole) piperazine, 1.6 g (0.04 mole) sodium hydroxide and 4.78 g (0.02 mole) sebacoyl

chloride. The yield was 3.10 g (61.02%). ( $T_m = 180^\circ\text{C dec}$ )  $[\eta] = 0.61$  (m-cresol,  $39^\circ\text{C}$ )

ir(KBr):  $3300\text{ cm}^{-1}$  (NH);  $2900\text{ cm}^{-1}$  (OH, acid);  $1730\text{ cm}^{-1}$  (C=O, acid);  $1670\text{ cm}^{-1}$  (C=O, amide).

nmr(TFA)  $\delta$  4.08 (m, 8,  $\text{CH}_2$ ); 2.72 (m, 4,  $\text{COCH}_2$ ); 1.5 (m, 12,  $\text{CH}_2$ )

Anal. Calcd. for  $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_2$  (repeating unit): C, 66.67; H, 9.52; N, 11.11.

Found: C, 67.50; H, 9.66; N, 10.97.

Preparation of poly(sebacoyl 2-methyl-1,2-propanediamide) (6).<sup>48</sup>

In a three-necked 500 ml round-bottomed flask equipped with a mechanical stirrer, dropping funnel with calcium chloride drying tube and reflux condenser was dissolved 3.97 g (0.045 mole) 2-methyl-1,2-diaminopropane in 50 ml ethanol-free chloroform. A mixture of 11.1 g (0.1 mole) triethylamine in 10 ml chloroform was added with stirring in an ice bath. Dropwise addition of 10.7 g (0.045 mole) sebacoyl chloride in 10 ml chloroform produced a precipitate, which dissolved as the reaction proceeded. When the evolution of heat subsided, the solution was poured into 400 ml hexane and a precipitate formed. It was filtered and washed with 1N HCl 50% acetone and distilled water. Washing produced a sticky polymer which was dried in the vacuum oven 48 hours at  $50^\circ\text{C}$ . The yield was 4.79 g (42.02%). ( $T_m = 73-85^\circ\text{C}$ )  $[\eta] = .06$  (m-cresol,  $39^\circ\text{C}$ )

ir(film):  $2600-3400\text{ cm}^{-1}$  (NH, OH, acid, broad);  $1600-1700\text{ cm}^{-1}$  (C=O, amide, C=O, acid, broad).

nmr(TFA)  $\delta$  8.6, 8.85, 7.0 (NH,  $\text{NH}_2$ ); 3.85 (s, 2,  $\text{CH}_2$ ); 2.6 (m, 4,  $\text{CH}_2$ ); 1.6 (m, 12,  $\text{CH}_2$ ); 1.45 (s, 6,  $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{26}\text{N}_2\text{O}_2$  (repeating unit): C, 66.14; H, 10.59; N, 11.14.

10.24; N, 11.02.

Found: C, 62.79; H, 10.48; N, 11.03.

Preparation of 4,4'-bis(chloroacetyl)diphenyl ether (15). The synthesis was that of Neville and Mahoney.<sup>40</sup> Into a 500 ml round-bottomed flask equipped with a magnetic stirrer, dropping funnel and calcium chloride drying tube and connected to the aspirator was introduced 50 ml methylene chloride. As vigorous stirring was maintained, 58 g (0.434 mole) anhydrous aluminum chloride and 43.4 g (0.38 mole) chloroacetyl chloride. The mixture was cooled to  $-10^{\circ}\text{C}$  in a sodium chloride ice bath. A solution of 29.45 g (0.173 mole) diphenyl ether in 20 ml methylene chloride was added dropwise over 30 minutes. The mixture was allowed to warm slowly to room temperature and was stirred for a total of 24 hours. The mixture was poured slowly into 200 g ice in the hood. A pale green precipitate formed. Enough methylene chloride was added to dissolve the precipitate and the mixture was transferred to a separatory funnel. The methylene chloride layer was separated and the aqueous layer was extracted with a small amount of methylene chloride. The aqueous layer was discarded and the combined methylene chloride extracts were washed with distilled water until the pH of the water layer was 7. The methylene chloride layer was dried with anhydrous magnesium chloride and evaporated. A gold solid remained. The bis(chloroacetyl)diphenyl ether was recrystallized three times with decolorizing to yield 32.82 g (58.73%) (15). (m.p. 108-109.5; lit<sup>40</sup>  $114^{\circ}\text{C}$ ).

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s);  $1590, 1500, 1000, 790\text{ cm}^{-1}$  (Ar);  $1200\text{ cm}^{-1}$  (C-O,b);  $775\text{ cm}^{-1}$  (C-Cl,m).

nmr(CDCl<sub>3</sub>)  $\delta$  7.1-8.25 (q,8,Ar); 4.75 (s,4,CH<sub>3</sub>).

Anal. Calcd. for:  $C_{16}H_{12}Cl_2O_3$ : C, 59.44; H, 3.72; Cl, 21.98.

Found: C, 60.01; H, 3.90; Cl, 22.30.

Preparation of 4,4'-bis(bromoacetyl)diphenyl ether (16). This compound was prepared as above using 43.42 g (0.326 mole) anhydrous aluminum chloride in 40 ml  $CH_2Cl_2$ , 57.53 g bromoacetyl bromide (0.285 mole) and 22.1 g (0.13 mole) diphenyl ether in 15 ml methylene chloride. The yield was 28.19 g (52.69%) cream-colored solid (m.p. 117.5-120°C; lit<sup>49,50</sup> 121°C, 124°C).

ir(KBr): 1680  $cm^{-1}$  (C=O); 1590, s, 1500, m, 1000, m (Ar); 1250  $cm^{-1}$  (C-O).

nmr( $CDCl_3$ )  $\delta$  7.2-8.3 (q, 8, Ar);  $\delta$  4.5 (s, 4,  $CH_2$ ).

Anal. Calcd. for:  $C_{16}H_{12}Br_2O_3$ : C, 46.60; H, 2.91; Br, 38.83.

Found: C, 46.88; H, 3.80; Br, 39.20.

Preparation of 4,4'-bis(2-bromopropionyl)diphenyl ether (17).

This compound was prepared in a similar manner using 28.98 g (0.22 mole) anhydrous aluminum chloride, 32.57 g (0.19) 2-bromopropionyl chloride in 25 ml methylene chloride and 14.73 g (0.087 mole) diphenyl ether in 10 ml methylene chloride. The yield was 23.79 g (62.44%) pale yellow solid. (m.p. 106-112°C).

ir(KBr): 1690  $cm^{-1}$  (C=O, s); 1580, 1495  $cm^{-1}$  (Ar, s); 1210  $cm^{-1}$  (C-O, s).

nmr( $CDCl_3$ )  $\delta$  7.1-8.3 (q, 8, Ar); 5.3 (q, 2, CH); 1.9 (d, 6,  $CH_3$ ).

Anal. Calcd. for:  $C_{18}H_{16}Br_2O_3$ : C, 49.09; H, 3.64; Br, 36.36.

Found: C, 49.33; H, 3.79; Br, 36.79.

Preparation of 4,4'-bis(2-chloropropionyl)diphenyl ether (18).

This compound was prepared as above using 80 g (0.6 mole) anhydrous

aluminum chloride, 51.68 g (0.41 mole) 2-chloropropionyl chloride and 34 g (0.2 mole) diphenyl ether. The yield was 18.06 g (25.73%) pale yellow solid. (m.p. 87.5-92.5°C)

ir(KBr): 1700  $\text{cm}^{-1}$  (C=O,s); 1590, 1500  $\text{cm}^{-1}$  (Ar,s); 1200  $\text{cm}^{-1}$  (C-O,s); 775  $\text{cm}^{-1}$  (C-Cl,s).

nmr( $\text{CDCl}_3$ )  $\delta$  7.1-8.2 (q,8,Ar); 5.2 (q,2,CH); 1.85 (d,6, $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}_3$ : C, 61.54; H, 4.56; Cl, 20.23.

Found: C, 61.32; H, 4.82; Cl, 19.94.

Preparation of 2-bromo-p-methoxypropiofenone (39). This compound was prepared in a similar manner using 13.35 g (0.01 mole) anhydrous aluminum chloride, 21.6 g (0.01 mole) 2-bromopropionyl bromide in 15 ml methylene chloride and 10.8 g (0.01 mole) anisole in 15 ml methylene chloride. The yield was 8.09 g (33.29%). (m.p. 64.5-66.5°C; lit<sup>51</sup> 66-67°C)

ir(NaCl): 1650  $\text{cm}^{-1}$  (C=O,s); 1500-1600, 1150, 1000, 850  $\text{cm}^{-1}$  (Ar); 1225  $\text{cm}^{-1}$  (C-O, s).

nmr( $\text{CDCl}_3$ )  $\delta$  6.8-8.2 (q,4,Ar); 5.35 (q,1,CH); 3.95 (s,3, $\text{OCH}_3$ ); 1.95 (d,3, $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{11}\text{BrO}_2$ : C, 49.38; H, 4.53; Br, 32.92.

Found: C, 49.66; H, 4.79; Br, 32.41.

Preparation of polyamine (19). In a 250 ml Erlenmeyer flask equipped with a magnetic stirrer was dissolved 3.23 g (0.01 mole) 4,4'-bis(chloroacetyl)diphenyl ether and 1.72 g (0.02 mole) piperazine in 100 ml hexamethylphosphoramide. The solution was placed in an oil bath and heated to 80°C. That temperature was maintained for one hour and then the flask was cooled in the bath and allowed to sit overnight. The piperazine hydrochloride which precipitated was filtered off and

the filtrate was poured into 1 l acetone with stirring. The precipitated polymer was filtered, washed with acetone, distilled water and 0.5 M ammonium hydroxide and dried under vacuum at 50°C 48 hours. The yield was 1.08 g (32.14%). ( $T_m = 160^\circ\text{C}$  dec)  $[\eta] = 0.21$  (m-cresol, 38.4°C)

ir(KBr):  $2800\text{ cm}^{-1}$  ( $R_2\text{NH}_2^+$ , s);  $1700\text{ cm}^{-1}$  (C=O, s);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA) 7.1-8.3 (q, 8, Ar); 5.2 (broad, 4,  $\text{CH}_2$ ); 4.2 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 59.01; H, 5.62; N, 7.46.

Preparation of polyamine (20). In a similar manner was prepared polyamine (20) using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl) diphenyl ether and 5.17 g (0.06 mole) piperazine in 100 ml N-methylpyrrolidone. The yield was 6.52 g (64.68%) gold solid. ( $T_m = 165^\circ\text{C}$  dec)  $[\eta] = 0.21$  (m-cresol, 39°C)

ir(KBr):  $2610\text{--}2780\text{ cm}^{-1}$  ( $R_2\text{NH}_2^+$ , s);  $2400\text{--}2500\text{ cm}^{-1}$  ( $R_3\text{NH}^+$ , m);  $1680\text{ cm}^{-1}$  (C=O, s); 1540, 1495, 820-840  $\text{cm}^{-1}$  (Ar);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.3 (q, 8, Ar); 5.25 (s, 4,  $\text{CH}_2$ ); 3.9-4.65 (broad m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 63.43; H, 6.16; N, 8.04.

Preparation of polyamine (21). This polymer was prepared in a similar manner using 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 1.72 g (0.02 mole) piperazine, 0.74 g (0.01 mole) lithium carbonate and 200 ml N-methylpyrrolidone. The yield was 0.74 g (11.01%)

gold polymer. ( $T_m = 175^\circ\text{C dec}$ )  $[\eta] = 0.24$  (m-cresol,  $39^\circ\text{C}$ )

nmr(TFA)  $\delta$  7.1-8.5 (q, 8, Ar); 5.25 (s, 4,  $\text{CH}_2$ ); 4.35 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 63.42; H, 6.16; N, 8.04.

Preparation of polyamine (22). This polymer was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 3.87 g (0.045 mole) piperazine and 0.55 g (0.0075 mole) lithium carbonate in 200 ml N-methylpyrrolidone. The yield was 3.55 g (35.22%).

( $T_m = 180^\circ\text{C dec}$ )  $[\eta] = 0.29$  (m-cresol,  $39^\circ\text{C}$ )  $\bar{M}_n = 1900$ .

ir(KBr):  $2550\text{--}2975\text{ cm}^{-1}$  ( $\text{R}_2\text{NH}_2^+$ , s);  $2350\text{--}2550\text{ cm}^{-1}$  ( $\text{R}_3\text{NH}$ , m);  $1690\text{ cm}^{-1}$  (C=O, s);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.6 (q, 8, Ar); 5.3 (s, 4,  $\text{CH}_2$ ); 4.3 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 65.66; H, 5.87; N, 8.33.

Preparation of polyamine (23). Polyamine (23) was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 2.58 g (0.03 mole) piperazine and 0.55 g (0.0075 mole) lithium carbonate in 200 ml N,N-dimethylacetamide. The yield was 0.28 g (2.78%) gold polymer. ( $T_m = 200^\circ\text{C dec}$ )

ir(KBr):  $3300\text{ cm}^{-1}$  ( $\text{R}_2\text{NH}$ , m);  $2350\text{--}3000\text{ cm}^{-1}$  ( $\text{R}_3\text{NH}^+$ ,  $\text{R}_2\text{NH}_2^+$ , m-s);  $1700\text{ cm}^{-1}$  (C=O, s);  $1210\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.3 (q, 8, Ar); 5.25 (s, 4,  $\text{CH}_2$ ); 3.8-4.6 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 61.26; H, 5.91; N, 6.90.

Preparation of polyamine (28). In a similar manner was prepared polyamine (28) using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)-diphenyl ether, 6.12 g (0.06 mole) N,N'-dimethyl-1,3-propanediamine and 150 ml hexamethylphosphoramide. The yield was 2.0 g (18.94%) gold polymer. ( $T_m = 140^\circ\text{C}$  dec)  $[\eta] = 0.10$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $2800\text{--}2950\text{ cm}^{-1}$  ( $R_2\text{NH}_2^+, s$ );  $2350\text{--}2550\text{ cm}^{-1}$  ( $R_3\text{NH}^+, m$ );  $1700\text{ cm}^{-1}$  (C=O, s);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.5 (q, 8, Ar); 5.0 (s, 4,  $\text{CH}_2$ ); 2.2-4.0 (broad, 12,  $\text{CH}_2, \text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3$  (repeating unit): C, 71.59; H, 6.82; N, 7.95.

Found: C, 62.72; H, 6.61; N, 7.68.

Preparation of polyamine (30). Polyamine (30) was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 12.62 g (0.06 mole) 4,4'-trinethylenedipiperidine in 200 ml N-methylpyrrolidone. The yield was 10.52 g (76.18%). ( $T_m = 130^\circ\text{C}$  dec)  $[\eta] = 0.21$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $2550\text{--}2950\text{ cm}^{-1}$  ( $R_2\text{NH}_2^+, s$ );  $2450\text{--}2550\text{ cm}^{-1}$  ( $R_3\text{NH}^+, m$ );  $1710\text{ cm}^{-1}$  (C=O, s);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA) 7.1-8.3 (q, 8, Ar); 4.85 (s, 4,  $\text{CH}_2$ ); 2.7-4.1 (m, 8,  $\text{CH}_2$ ); 1.1-2.4 (m, 16,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_3$  (repeating unit): C, 75.65; H, 7.83; N, 6.09.

Found: C, 72.87; H, 8.11; N, 6.09.

Preparation of polyamine (24). In a three-necked 500 ml round-bottomed flask equipped with a nitrogen inlet and a magnetic stirrer were dissolved 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether

and 3.87 g (0.045 mole) piperazine in 200 ml N-methylpyrrolidone. The mixture was stirred and 0.55 g (0.0075 mole) lithium carbonate was added. The flask was heated to 90°C in an oil bath and that temperature was maintained for three hours. The flask was cooled in the bath under nitrogen and was allowed to sit overnight at room temperature. The solid precipitate was filtered off and the filtrate was poured with stirring into approximately 3.5 l acetone. The polymer was filtered, washed with acetone, 0.5 M ammonium hydroxide and distilled water and dried 48 hours at 50°C under vacuum. The yield was 5.66 g (56.15%). ( $T_m = 160^\circ\text{C}$  dec)  $[\eta] = 0.12$  (m-cresol, 38.4°C)

ir(KBr): 2450-2820  $\text{cm}^{-1}$  ( $R_3\text{NH}^+$ ,  $R_2\text{NH}_2^+$ , m-s); 1700  $\text{cm}^{-1}$  (C=O, s); 1590  $\text{cm}^{-1}$  (Ar, s); 1200  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.2-8.5 (q, 8, Ar); 5.2 (s, 4,  $\text{CH}_2$ ); 4.25 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 60.59; H, 6.00; N, 6.88.

Preparation of polyamine (25). Polyamine (25) was prepared by a similar procedure using 1.94 g (0.006 mole) 4,4'-bis(chloroacetyl) diphenyl ether, 0.77 g (0.009 mole) piperazine and 0.27 g (0.003 mole) lithium carbonate in 50 ml N-methylpyrrolidone. The yield was 1.24 g (61.39%). ( $T_m = 150^\circ\text{C}$  dec)  $[\eta] = 0.14$  (m-cresol, 38.4°C)

ir(KBr): 2300-2900  $\text{cm}^{-1}$  ( $R_3\text{NH}^+$ ,  $R_2\text{NH}_2^+$ , m-s); 1700  $\text{cm}^{-1}$  (C=O, s); 1570, 1490  $\text{cm}^{-1}$  (Ar); 1210  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  6.9-8.4 (q, 8, Ar); 5.2 (s, 4,  $\text{CH}_2$ ); 3.5-4.8 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 66.13; H, 5.97; N, 8.60.

Preparation of polyamine (26). This polymer was prepared in a similar manner using 1.94 g (0.006 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 0.57 g (0.0066 mole) piperazine and 1.33 g (0.0132 mole) triethylamine in 50 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 1.69 g (83.66%). ( $T_m = 160^\circ\text{C dec}$ )  $[\eta] = 0.22$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $2340\text{--}2900\text{ cm}^{-1}$  ( $R_3\text{NH}^+, R_2\text{NH}_2^+, m-s$ );  $1690\text{ cm}^{-1}$  (C=O, s);  $1580, 1505\text{ cm}^{-1}$  (Ar, s);  $1200\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.4 (q, 8, Ar); 5.2 (s, 4,  $\text{CH}_2$ ); 3.7-4.6 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 65.83; H, 5.75; N, 8.26.

Preparation of polyamine (27). This polymer was prepared in a similar manner using 1.94 g (0.006 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 0.77 g (0.009 mole) piperazine and 0.11 g (0.0015 mole) lithium carbonate in 50 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 0.91 g (45.05%). ( $T_m = 150^\circ\text{C dec}$ )  $[\eta] = 0.17$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $3400\text{ cm}^{-1}$  (NH, m);  $2320\text{--}2900\text{ cm}^{-1}$  ( $R_3\text{NH}^+, R_2\text{NH}_2^+, m-s$ );  $1690\text{ cm}^{-1}$  (C=O, s);  $1590, 1515\text{ cm}^{-1}$  (Ar, s);  $1210\text{ cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.2-8.9 (q, 8, Ar); 5.2 (s, 4,  $\text{CH}_2$ ); 4.0-5.7 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 69.91; H, 6.21; N, 8.60.

Preparation of polyamine (29). This polymer was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 4.59 g (0.045 mole) N,N'-dimethylpropanediamine (fractionally

distilled) and 0.55 g (0.0074 mole) lithium carbonate in 200 ml N-methylpyrrolidone. The yield was 4.68 g (44.32%). ( $T_m = 180^\circ\text{C}$  dec). This polymer was insoluble in m-cresol. The presence of trace amounts of primary amine would cause crosslinking.

ir(KBr): 2390-2920  $\text{cm}^{-1}$  ( $\text{R}_3\text{NH}^+, \text{R}_2\text{NH}_2^+, \text{m-s}$ ); 1670  $\text{cm}^{-1}$  (C=O, s); 1580, 1495  $\text{cm}^{-1}$  (Ar, s); 1210  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA) 7.1-8.8 (q, 8, Ar); 5.1 (s, 4,  $\text{CH}_2$ ); 2.1-4.3 (m, 12,  $\text{CH}_2, \text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3$  (repeating unit): C, 71.59; H, 6.82; N, 7.95.

Found: C, 69.54; H, 6.02; N, 5.07.

Preparation of polyamine (31). This polymer was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 9.47 g (0.045 mole) 4,4'-trimethylenedipiperidine and 0.55 g (0.0074 mole) lithium carbonate in 200 ml N-methylpyrrolidone. The yield was 10.03 g (72.68%). ( $T_m = 150^\circ\text{C}$  dec)  $[\eta] = 0.15$  (m-cresol,  $38.4^\circ\text{C}$ )  $\bar{M}_n = 1600$

ir(KBr): 2400-2900  $\text{cm}^{-1}$  ( $\text{R}_3\text{NH}^+, \text{R}_2\text{NH}_2^+, \text{m-s}$ ); 1695  $\text{cm}^{-1}$  (C=O, s); 1580, 1500  $\text{cm}^{-1}$  (Ar, s); 1210  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA):  $\delta$  7.1-8.4 (q, 8, Ar); 4.8 (s, 4,  $\text{CH}_2$ ); 2.8-4.1 (m, 8,  $\text{CH}_2$ ); 1.0-2.4 (m, 16,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_3$  (repeating unit): C, 75.65; H, 7.83; N, 6.09.

Found: C, 71.06; H, 6.52; N, 5.86.

Preparation of polyamine (32). Polyamine (32) was prepared in a similar manner using 8.24 g (0.02 mole) 4,4'-bis(bromoacetyl)diphenyl ether, 2.58 g (0.03 mole) piperazine and 0.37 g (0.005 mole) lithium

carbonate in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 4.08 g (60.71%). ( $T_m = 155^\circ\text{C}$ )  $[\eta] = 0.20$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $2400\text{--}2900\text{ cm}^{-1}$  ( $R_3\text{NH}^+, R_2\text{NH}_2^+, \text{m-s}$ );  $1700\text{ cm}^{-1}$  ( $\text{C=O, s}$ );  $1580\text{ cm}^{-1}$  (Ar);  $1200\text{ cm}^{-1}$  ( $\text{C-O, s}$ ).

nmr(TFA)  $\delta$  7.1-8.4 (q, 8, Ar); 5.2 (s, 4,  $\text{CH}_2$ ); 3.8-4.8 (m, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$  (repeating unit): C, 71.43; H, 5.95; N, 8.33.

Found: C, 66.38; H, 6.09; N, 8.28.

Preparation of polyamine (33). This polymer was prepared in a similar manner using 8.24 g (0.02 mole) 4,4'-bis(bromoacetyl)diphenyl ether, 6.31 g (0.03 mole) trimethylenedipiperidine and 0.37 g (0.005 mole) lithium carbonate in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 7.05 g (76.63%). ( $T_m = 200^\circ\text{C}$  dec)  $[\eta] = 0.21$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $2300\text{--}2900\text{ cm}^{-1}$  ( $R_3\text{NH}^+, R_2\text{NH}_2^+, \text{m-s}$ );  $1690\text{ cm}^{-1}$  ( $\text{C=O, s}$ );  $1580, 1500\text{ cm}^{-1}$  (Ar, s);  $1220\text{ cm}^{-1}$  ( $\text{C-O, s}$ ).

nmr(TFA)  $\delta$  7.1-8.55 (q, 8, Ar); 4.9 (s, 4,  $\text{CH}_2$ ); 3.0-4.2 (m, 8,  $\text{CH}_2$ ); 1.0-2.8 (m, 16,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_3$  (repeating unit): C, 75.65; H, 7.83; N, 6.09.

Found: C, 69.36; H, 7.93; N, 5.58.

Preparation of polyamine (34). This polymer was prepared in a similar manner using 8.8 g (0.02 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 2.58 g (0.03 mole) piperazine and 0.37 g (0.005 mole) lithium carbonate in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 2.25 g (30.91%). ( $T_m = 140^\circ\text{C}$  dec)

$[\eta] = 0.09$  (m-cresol, 38.4°C)

ir(KBr): 2300-2900  $\text{cm}^{-1}$  ( $\text{R}_3\text{NH}^+$ ,  $\text{R}_2\text{NH}_2^+$ , m-s); 1690  $\text{cm}^{-1}$  (C=O, s); 1580, 1495  $\text{cm}^{-1}$  (Ar, s); 1210  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.15-8.45 (q, 8, Ar); 5.5 (m, 2, CH); 4.15 (m, 8,  $\text{CH}_2$ ); 1.9 (d, 6,  $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3$  (repeating unit): C, 92.53; H, 6.59; N, 7.69.

Found: C, 66.15; H, 6.89; N, 8.06.

Preparation of polyamine (35). Polyamine (35) was prepared in the same way using 8.8 g (0.02 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 6.31 g (0.03 mole) 4,4'-trimethylenedipiperidine and 0.37 g (0.005 mole) lithium carbonate in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 6.88 (70.49%). ( $T_m = 170^\circ$  dec)  $[\eta] = 0.15$  (m-cresol, 38.4°C)

ir(KBr): 2300-2900  $\text{cm}^{-1}$  ( $\text{R}_3\text{NH}^+$ ,  $\text{R}_2\text{NH}_2^+$ , m-s); 1670  $\text{cm}^{-1}$  (C=O, s); 1590, 1495  $\text{cm}^{-1}$  (Ar, s); 1210  $\text{cm}^{-1}$  (C-O, s).

nmr(TFA)  $\delta$  7.1-8.6 (q, 8, Ar); 5.2 (m, 2,  $\text{CH}_2$ ); 2.8-4.3 (m, 8,  $\text{CH}_2$ ); 0.8-2.8 (m, 22,  $\text{CH}_2$ ,  $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{31}\text{H}_{40}\text{N}_2\text{O}_3$  (repeating unit): C, 76.23; H, 8.20; N, 5.74.

Found: C, 69.89; H, 8.19; N, 5.56.

Preparation of poly(amine-urea) (36). To 100 ml dry N-methylpyrrolidone in a 500 ml round-bottomed flask equipped with nitrogen inlet, calcium chloride drying tube and magnetic stirrer, was added 4 g polyamine (30), 1.0 g (0.006 mole) 1,6-diisocyanatohexane and 5 drops dibutyl tin diacetate. The mixture was heated 24 hours under nitrogen at 80°C and then cooled under nitrogen. The solution was poured into

approximately 1 l distilled water with stirring. The polymer was allowed to settle, was filtered and washed with distilled water. It was dried under vacuum 48 hours at 50°C. The yield was 4.22 g pale yellow polymer. ( $T_m = 140^\circ\text{C}$  dec). This polymer could not be completely dissolved by trifluoroacetic acid or m-cresol.  $\bar{M}_n = 1800$ .

ir(KBr):  $3600\text{ cm}^{-1}$  (NH,m);  $1620\text{--}1760\text{ cm}^{-1}$  (C=O,s,ketone, acid,urea).

nmr(TFA)  $\delta$  7.1-8.5 (q,8,Ar); 4.85 (s,4,CH<sub>2</sub>); 2.8-4.2 (m,CH<sub>2</sub>); 0.9-2.6 (m,CH<sub>2</sub>).

Anal. Found: C, 67.05; H, 7.45; N, 8.36. Based on nitrogen analysis, there are one to two diisocyanate units for every repeating unit of polyamine (30).

Preparation of extended polyester (53). This polymer was prepared in a similar way using 2 g polyester (44), 0.5 g (0.003 mole) 1,6-diisocyanatohexane, 100 ml dry N-methylpyrrolidone and 5 drops triethylamine. The yield was 1.91 g tan polymer. ( $T_m = 180\text{--}187^\circ\text{C}$ )  $[\eta] = 0.64$  (m-cresol, 38.4°C)

ir(KBr):  $3300\text{ cm}^{-1}$  (NH,m);  $1630\text{--}1750\text{ cm}^{-1}$  (C=O,s,ketone, mixed anhydride, acid).

nmr(TFA)  $\delta$  7.1-8.3 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl); 1.4-4.1 (m,CH<sub>2</sub>).

Anal. Found: C, 67.89; H, 5.87; N, 1.50. Based on nitrogen analysis, there is one diisocyanate unit incorporated for every four repeating units of polymer (44).

Preparation of model compound (37). In a 100 ml round-bottomed flask were mixed 8 g  $\alpha$ -bromo-p-methoxyacetophenone (0.035 mole), 3.01 g (0.035 mole) piperazine in 35 ml N-methylpyrrolidone. The flask was

warmed on the steam bath for 6 hours and the contents were poured into 300 ml 0.5 M ammonium hydroxide with stirring. The solid was filtered, washed with distilled water and dried under vacuum 48 hours at 50°C.

The yield was 1.48 g (22.12%). (m.p. 145-154°C)

ir(KBr): 2800  $\text{cm}^{-1}$  ( $\text{CH}_2\text{N}, \text{s}$ ); 1700  $\text{cm}^{-1}$  ( $\text{C=O}, \text{s}$ ); 1590  $\text{cm}^{-1}$  ( $\text{Ar}, \text{s}$ ); 1250  $\text{cm}^{-1}$  ( $\text{CH}_3\text{OAr}, \text{s}$ ).

nmr(TFA)  $\delta$  6.75-8.25 (q, 8, Ar); 3.9 (s, 6,  $\text{CH}_3\text{O}$ ); 3.8 (s, 4,  $\text{CH}_2$ ); 2.75 (s, 8,  $\text{CH}_2$ ).

Anal. Calcd. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$ : C, 69.11; H, 6.81; N, 7.33.

Found: C, 69.31; H, 6.75; N, 7.38.

Preparation of model compound (38). This material was prepared in two ways. (1) In the first method an attempt was made to prepare  $\alpha$ -chloro-p-methoxypropionophenone. The procedure was similar to that used for 4,4'-bis(chloroacetyl)diphenyl ether (15) using 12.1 g (0.09 mole) anhydrous aluminum chloride, 11.5 g (0.09 mole) 2-chloropropionyl chloride and 9.78 g (0.09 mole) anisole in 20 ml methylene chloride. This compound is a low melting material, which could not be recrystallized and is also a SEVERE skin irritant. It was thus used as is in the following procedure. This material (assuming 50% yield), as well as 3.5 g (0.04 mole) piperazine was dissolved in 40 ml N-methylpyrrolidone and warmed on the steam bath 12 hours. The resulting slurry was poured into 300 ml 0.5 M ammonium hydroxide with stirring. An oil formed, which on drying under vacuum 48 hours at 50°C, became solid. It was recrystallized three times from 2-propanol to yield 0.61 g (7.44%) cream-colored solid. (m.p. 138-145°C).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$ : C, 70.24; H, 7.32; N, 6.83.

Found: C, 69.96; H, 7.47; N, 6.63.

(2) The procedure above in N-methylpyrrolidone was repeated using 4.86 g (0.02 mole)  $\alpha$ -bromo-p-methoxypropiofenone (39), 1.72 g (0.02 mole) piperazine and 25 ml N-methylpyrrolidone. The yield was 0.88 g (21.46%). (m.p. 132-138°C)

ir(KBr): 2800  $\text{cm}^{-1}$  ( $\text{CH}_2\text{N}, \text{m}$ ); 1660  $\text{cm}^{-1}$  ( $\text{C=O}, \text{s}$ ); 1590  $\text{cm}^{-1}$  ( $\text{Ar}, \text{s}$ ); 1240  $\text{cm}^{-1}$  ( $\text{C-O}, \text{s}$ ).

nmr( $\text{CDCl}_3$ )  $\delta$  6.7-8.3 (q, 8, Ar); 3.9 (s, q, 8,  $\text{CH}_3\text{O}, \text{CHN}$ ); 2.6 (s, 8,  $\text{CH}_2$ ); 1.25 (d, 6,  $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$ : C, 70.24; H, 7.32; N, 6.83.

Found: C, 70.06; H, 7.45; N, 6.74.

Preparation of polyester (39). Into a 250 ml Erlenmeyer flask were introduced 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 3.32 g (0.02 mole) terephthalic acid, 4.04 g (0.04 mole) triethylamine and 150 ml N,N-dimethylformamide. The mixture was swirled until all dissolved and the flask was placed in the refrigerator for 48 hours. The slurry which formed was poured into 1 l iced water with stirring. The precipitate was allowed to settle overnight and was collected with suction. It was washed with distilled water and acetone and dried in vacuo at 50°C 48 hours. The yield was 5.98 g (71.88%). ( $T_m$  = 230-260°C)

ir(KBr): 1695  $\text{cm}^{-1}$  ( $\text{CO}, \text{s}, \text{ketone}$ ); 1705  $\text{cm}^{-1}$  ( $\text{C=O}, \text{s}, \text{ester}$ ); 1590, 1500  $\text{cm}^{-1}$  ( $\text{Ar}, \text{s}$ ); 1215  $\text{cm}^{-1}$  ( $\text{C-O}, \text{s}$ ).

nmr(TFA)  $\delta$  8.5 (s, 4, Ar); 7.1-8.5 (q, 8, Ar); 6.0 (s, 4,  $\text{CH}_2\text{O}$ ); 4.95 (s,  $\text{CH}_2\text{Cl}$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{16}\text{O}_7$  (repeating unit): C, 69.23; H, 3.85.

Found: C, 68.09; H, 4.21.

Preparation of polyester (40). In a similar manner was prepared polyester (40) using 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 2.92 g (0.02 mole) adipic acid and 4.04 g (0.004 mole) triethylamine in 150 ml N,N-dimethylformamide. The yield was 6.18 g (78.03%). ( $T_m = 155^\circ\text{C}$ )  $[\eta] = 0.12$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $1700\text{ cm}^{-1}$  (C=O,s,ketone);  $1730\text{ cm}^{-1}$  (C=O,s,ester);  $1590\text{ cm}^{-1}$  (Ar);  $1210\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.3 (q,8,Ar); 6.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl); 2.75 (m,4,CH<sub>2</sub>); 1.9 (m,4,CH<sub>2</sub>).

Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>7</sub> (repeating unit): C, 66.67; H, 5.05.

Found: C, 66.50; H, 5.30.

Preparation of polyester (41). Polyester (41) was prepared in the same way using 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 2.92 g (0.02 mole) adipic acid and 4.04 g (0.04 mole) triethylamine in 150 ml N-methylpyrrolidone. The yield was 6.66 g (84.09%). ( $T_m = 165^\circ\text{C}$ )  $[\eta] = 0.20$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $1685\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  $1580\text{ cm}^{-1}$  (Ar);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl); 2.8 (m,4,CH<sub>2</sub>); 1.95 (m,4,CH<sub>2</sub>).

Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>7</sub> (repeating unit): C, 66.67; H, 5.05.

Found: C, 65.37; H, 5.34.

Preparation of polyester (42). This polymer was prepared in the same way using 6.46 (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 4.04 g (0.02 mole) sebacic acid and 4.04 g (0.04 mole) triethylamine in 150 ml N,N-dimethylformamide. The yield was 7.3 g (80.75%). ( $T_m = 165^\circ\text{C}$ )  $[\eta] = 0.15$  (m-cresol,  $38.4^\circ\text{C}$ ).

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1750\text{ cm}^{-1}$  (C=O,s,ester);  
 $1590\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.3 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.85 (s,CH<sub>2</sub>Cl);  
 2.7 (m,4,CH<sub>2</sub>); 1.5 (m,12,CH<sub>2</sub>).

Anal. Calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>7</sub> (repeating unit): C, 69.03; H, 6.19.

Found: C, 67.36; H, 6.28.

Preparation of polyester (43). In the same way was prepared polyester (43) using 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 3.76 g (0.02 mole) azelaic acid and 4.04 g (0.04 mole) triethylamine in 150 ml N-methylpyrrolidone. The yield was 7.87 g (89.84%).

(T<sub>m</sub> = 145-165°C)  $[\eta]$  = 0.21 (m-cresol, 38.4°C)

ir(KBr):  $1700\text{ cm}^{-1}$  (C=O,s,ketone);  $1750\text{ cm}^{-1}$  (C=O,s,ester);  
 $1590, 1510\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl);  
 2.75 (m,4,CH<sub>2</sub>); 1.7 (m,10,CH<sub>2</sub>).

Anal. Calcd. for C<sub>25</sub>H<sub>26</sub>O<sub>7</sub> (repeating unit): C, 68.49; H, 5.94.

Found: C, 68.43; H, 6.09.

Preparation of polyester (44). In a three-necked round-bottomed flask equipped with a nitrogen inlet and a magnetic stirrer were mixed 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 2.92 g (0.02 mole) adipic acid and 4.44 g (0.044 mole - 10% excess) triethylamine in 150 ml N-methylpyrrolidone. The flask was heated in an oil bath to 80°C and maintained at that temperature for 18 hours. The flask was cooled under N<sub>2</sub> and the solution was poured into approximately 1.5 l iced water with stirring. The pale yellow polymer gradually settled and was filtered. It was washed with water and acetone and dried under vacuum 48 hours at 50°C. The yield was 4.60 g (58.08%). (T<sub>m</sub> = 180°C)

$[\eta] = 0.24$  (m-cresol,  $38.4^{\circ}\text{C}$ )

ir(KBr):  $1695\text{ cm}^{-1}$  (C=O,s,ketone);  $1715\text{ cm}^{-1}$  (C=O,s,ester);  
 $1585\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.85 (s,CH<sub>2</sub>Cl<sub>1</sub>);  
 2.75 (m,4,CH<sub>2</sub>); 1.9 (m,4,CH<sub>2</sub>).

Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>7</sub> (repeating unit): C, 66.67; H, 5.05.

Found: C, 66.43; H, 5.27.

Preparation of polyester (45). This polyester was prepared in a similar manner using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 5.23 g (0.03 mole) suberic acid and 6.66 g (0.066 mole) triethylamine in 200 ml N-methylpyrrolidone. The yield was 9.53 g (74.92%).

( $T_m = 145^{\circ}\text{C}$ )  $[\eta] = 0.08$  (m-cresol,  $38.4^{\circ}\text{C}$ )

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1750\text{ cm}^{-1}$  (C=O,s,ester);  
 $1585\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl).

Anal. Calcd. for C<sub>24</sub>H<sub>24</sub>O<sub>7</sub> (repeating unit): C, 67.92; H, 5.66.

Found: C, 66.91; H, 5.70.

Preparation of polyester (46). The procedure above was repeated with 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 6.06 g (0.03 mole) sebacic acid and 6.66 g (0.066 mole) triethylamine in 200 ml N-methylpyrrolidone. The yield was 12.16 g (89.68%).

( $T_m = 150^{\circ}\text{C}$ )  $[\eta] = 0.15$  (m-cresol,  $38.4^{\circ}\text{C}$ )

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  
 $1585\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.15-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl);

2.4-2.9 (m,4,CH<sub>2</sub>); 1.2-2.1 (m,12,CH<sub>2</sub>).

Anal. Calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>7</sub> (repeating unit): C, 69.03; H, 6.19.

Found: C, 67.98; H, 6.30.

Preparation of polyester (47). This polyester was prepared in the same way using 9.69 g (0.03 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 6.91 (0.03 mole) 1,10-decanedicarboxylic acid and 6.66 g (0.066 mole) triethylamine in 200 ml N-methylpyrrolidone. The yield was 11.97 g (83.13%). ( $T_m = 150^\circ\text{C}$ )  $[\eta] = 0.15$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  $1580\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.7 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl); 2.4-2.95 (m,4,CH<sub>2</sub>); 1.2-2.25 (m,16,CH<sub>2</sub>).

Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>O<sub>7</sub> (repeating unit): C, 70.00; H, 6.67.

Found: C, 69.48; H, 6.80.

Preparation of polyester (48). This polyester was prepared using 8.24 g (0.02 mole) 4,4'-bis(bromoacetyl)diphenyl ether, 4.04 g (0.02 mole) sebacic acid and 4.44 g (0.044 mole) triethylamine in 150 ml N-methylpyrrolidone. The yield was 4.39 g (48.56%). ( $T_m = 155^\circ\text{C}$ )  $[\eta] = 0.15$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  $1590\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.65 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl).

Anal. Calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>7</sub> (repeating unit): C, 69.03; H, 6.19.

Found: C, 66.98; H, 6.64.

Preparation of polyester (49). Polyester (49) was prepared in a similar way using 8.24 g (0.02 mole) 4,4'-bis(bromoacetyl)diphenyl ether, 4.61 g (0.02 mole) 1,10-decanedicarboxylic acid and 4.44 g (0.044 mole) triethylamine in 150 ml N-methylpyrrolidone. The yield was 2.25 g sticky tan polymer (23.44%). ( $T_m = 95-140^\circ\text{C}$ )  $[\eta] = 0.07$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(NaCl): 1650-1735  $\text{cm}^{-1}$  (C=O,s,ketone,ester); 1200  $\text{cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.45 (q,8,Ar); 5.65 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl); 2.3-2.85 (m,4,CH<sub>2</sub>); 1.1-2.2 (m,16,CH<sub>2</sub>).

Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>O<sub>7</sub> (repeating unit): C, 70.00; H, 6.67.

Found: C, 54.31; H, 6.42.

Preparation of polyester (50). This polymer was prepared in a similar manner using 8.8 g (0.02 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 4.04 g (0.02 mole) sebacic acid and 4.44 g (0.044 mole) triethylamine in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 4.68 g (48.75%). This polymer is sticky at room temperature and is probably completely amorphous, at least partially due to the fact that the bis(propionyl)diphenyl ether exists as a mixture of isomers in the polymer.  $[\eta] = 0.12$  (m-cresol, 38.4°C)

ir(NaCl): 1670  $\text{cm}^{-1}$  (C=O,s,ketone); 1720  $\text{cm}^{-1}$  (C=O,s,ester); 1580  $\text{cm}^{-1}$  (Ar,s); 1210  $\text{cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.5 (q,8,Ar); 6.3 (q,2,CHO); 5.6 (q,CHCl); 2.2-2.9 (m,4,CH<sub>2</sub>); 1.0-2.1 (m,18,CH<sub>2</sub>,CH<sub>3</sub>).

Anal. Calcd for C<sub>28</sub>H<sub>32</sub>O<sub>7</sub> (repeating unit): C, 70.00; H, 6.67.

Found: C, 65.31; H, 6.57.

Preparation of polyester (51). In a similar way was prepared polyester (51) using 8.8 g (0.02 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 4.61 g (0.02 mole) 1, 10-decanedicarboxylic acid and 4.44 g (0.044 mole) triethylamine in 150 ml N-methylpyrrolidone. Heating was continued for 24 hours. The yield was 1.47 g (14.47%). This polymer is amorphous, as polyester (50).  $[\eta] = 0.13$  (m-cresol, 38.4°C)

ir(NaCl):  $1690\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  
 $1590\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 6.25 (q,2,CHO); 2.15-2.8  
 (m,4,CH<sub>2</sub>); 1.0-2.1 (m,16,CH<sub>2</sub>).

Anal. Calcd. for C<sub>30</sub>H<sub>36</sub>O<sub>7</sub> (repeating unit): C, 70.87; H, 7.09.

Found: C, 68.11; H, 6.80.

Preparation of polyester (52). This polymer was prepared in a similar manner using 3.23 g (0.01 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 2.22 g (0.011 mole) sebacic acid and 1.48 g (0.02 mole) lithium carbonate in 100 ml N-methylpyrrolidone. Heating was continued 24 hours. The yield was 3.68 g (81.42%). ( $T_m = 160^\circ\text{C}$ )  $[\eta] = 0.26$  (m-cresol,  $38.4^\circ\text{C}$ )

ir(KBr):  $1660\text{ cm}^{-1}$  (C=O,s,ketone);  $1740\text{ cm}^{-1}$  (C=O,s,ester);  
 $1580\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  7.1-8.4 (q,8,Ar); 5.65 (s,4,CH<sub>2</sub>O); 4.9 (s,CH<sub>2</sub>Cl);  
 2.3-2.9 (m,4,CH<sub>2</sub>); 1.2-2.2 (m,12,CH<sub>2</sub>).

Anal. Calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>7</sub> (repeating unit): C, 69.03; H, 6.19.

Found: C, 65.23; H, 6.13.

Preparation of model compound (54). This diester was prepared using the method of Sheehan and Umezawa<sup>43</sup> for similar compounds. In a 125 ml Erlenmeyer flask were mixed 6.46 g (0.02 mole) 4,4'-bis(chloroacetyl)diphenyl ether, 4.64 g (0.04 mole) hexanoic acid and 4.04 g (0.04 mole) triethylamine in 40 ml N,N-dimethylformamide. The flask was swirled until all dissolved and was placed in the refrigerator 24 hours. Then the contents were poured into 350 ml iced water with stirring. The white solid was filtered, washed with distilled water and dried in vacuo 48 hours at  $50^\circ\text{C}$ . Recrystallization twice from

2-propanol yielded 6.23 g (64.63%). (m.p. 118.5-120.5°C)

ir(KBr):  $1695\text{ cm}^{-1}$  (C=O,s,ketone);  $1725\text{ cm}^{-1}$  (C=O,s,ester);  
 $1175, 860\text{ cm}^{-1}$  (C-O,s).

nmr(CDCl<sub>3</sub>)  $\delta$  7.1-8.35 (q,8,Ar); 5.25 (s,4,CH<sub>2</sub>O); 2.2-2.7  
 (m,4,CH<sub>2</sub>); 0.7-2.0 (m,18,CH<sub>2</sub>,CH<sub>3</sub>).

Anal. Calcd. for C<sub>28</sub>H<sub>34</sub>O<sub>7</sub>: C, 69.71; H, 7.05.

Found: C, 69.75; H, 7.11.

Preparation of model compound (55). This compound was prepared in a similar manner using 4.40 g (0.01 mole) 4,4'-bis(2-bromopropionyl)diphenyl ether, 2.32 g (0.02 mole) hexanoic acid and 2.02 g (0.02 mole) triethylamine in 20 ml N-methylpyrrolidone. The product was a viscous oil. This material was purified using column chromatography on silica gel. Carbon tetrachloride, methylene chloride and methanol were eluting solvents. The pure material recovered weighed 3.25 g (63.73%).

ir(NaCl):  $1715\text{ cm}^{-1}$  (C=O,s,ester);  $1660\text{ cm}^{-1}$  (C=O,s,ketone);  
 $1585\text{ cm}^{-1}$  (Ar,s);  $1200\text{ cm}^{-1}$  (C-O,s).

nmr(TFA)  $\delta$  6.9-8.2 (q,8,Ar); 5.9 (q,2,CHO); 2.15-2.6  
 (m,4,CH<sub>2</sub>); 0.7-2.1 (m,24,CH<sub>2</sub>,CH<sub>3</sub>).

Anal. Calcd. for C<sub>30</sub>H<sub>38</sub>O<sub>7</sub>: C, 70.59; H, 7.45.

Found: C, 69.75; H, 7.28.

## V. REPRESENTATIVE SPECTRA

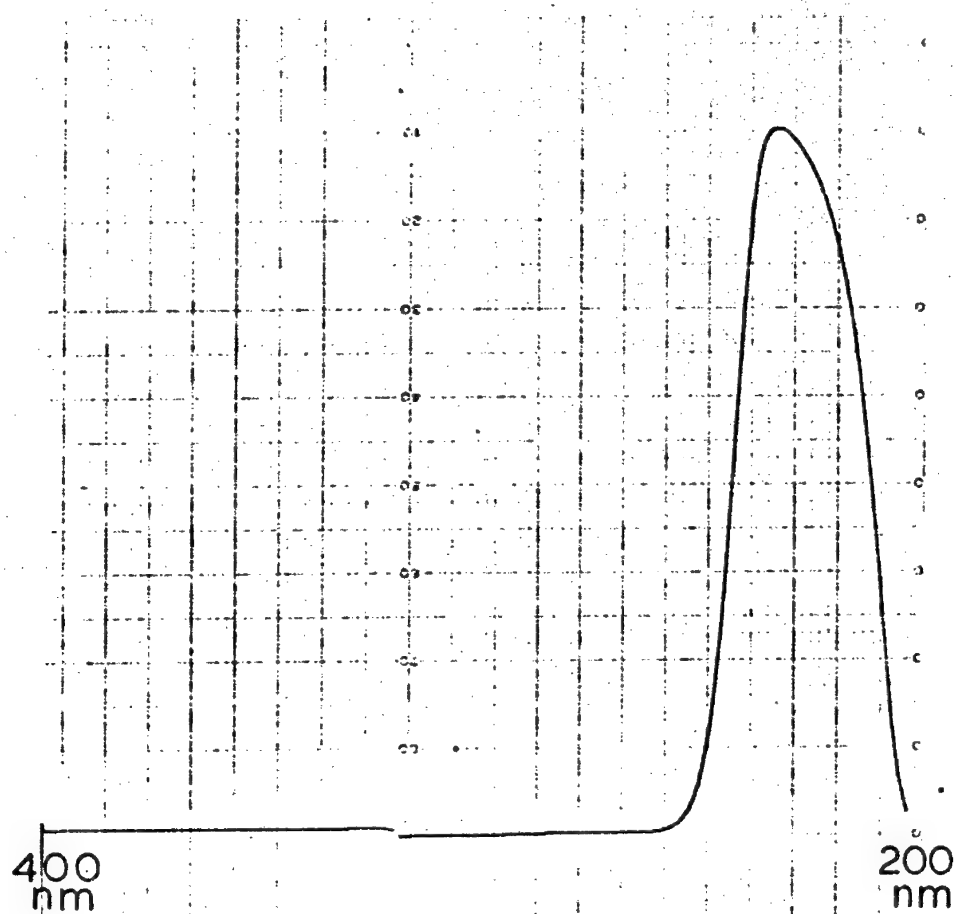


Figure 12. Ultraviolet Spectrum of Model Compound (1) in 95% Ethanol.

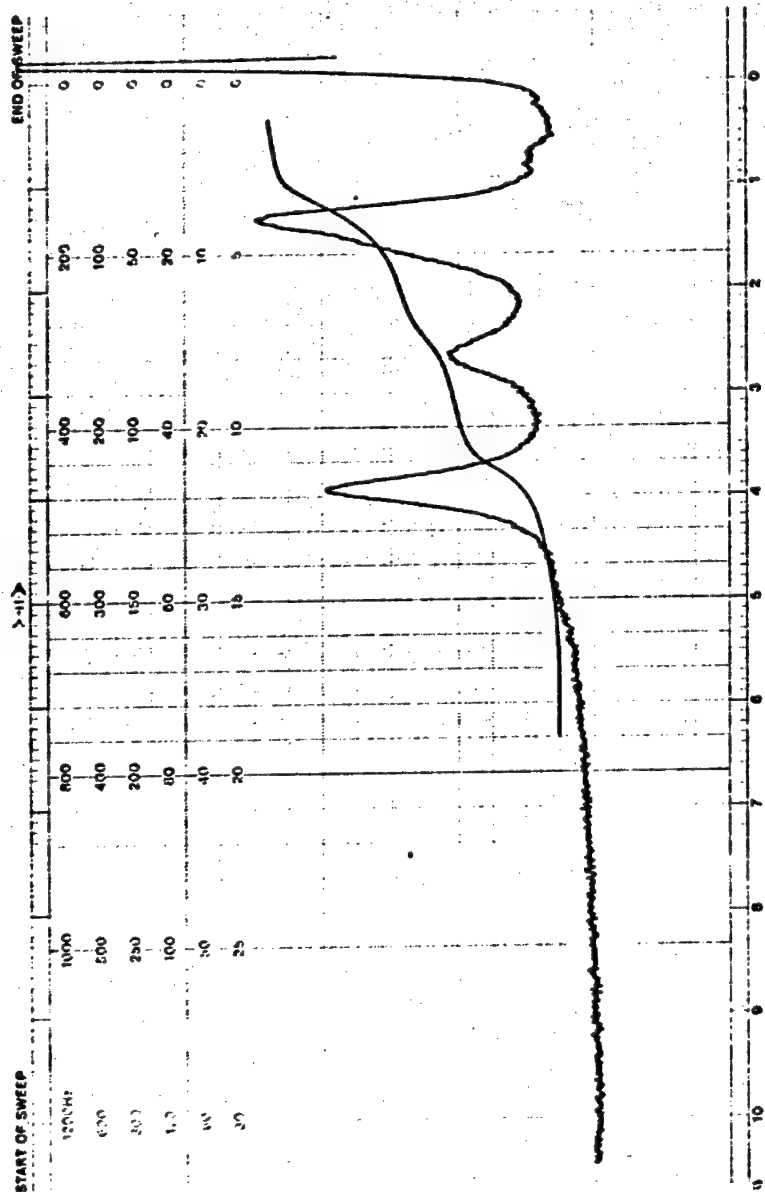


Figure 13. NMR of Polysebacamide (4).

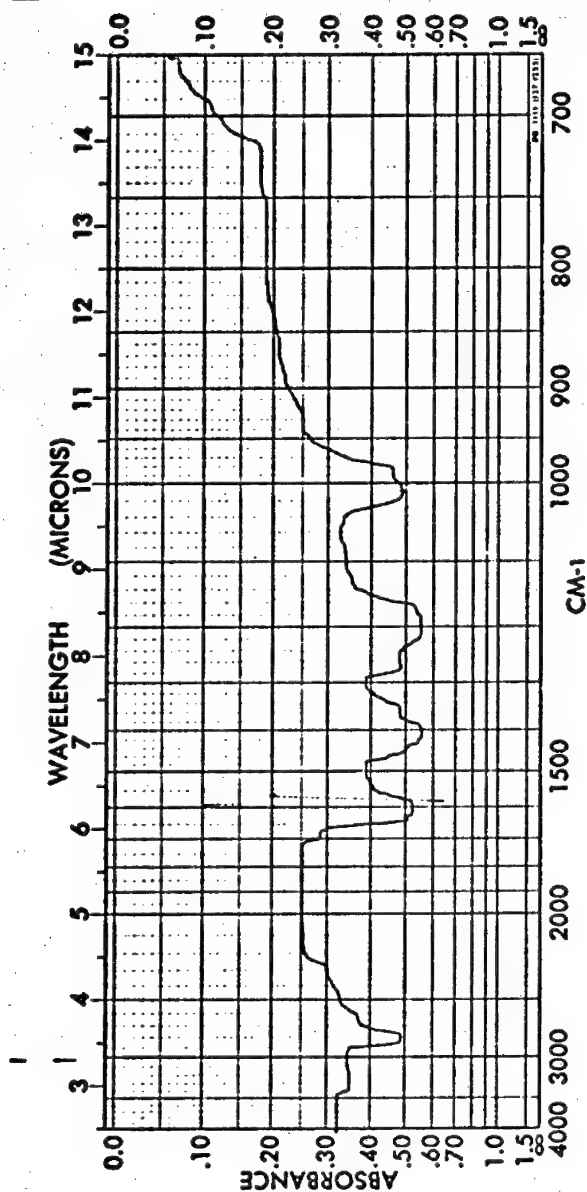
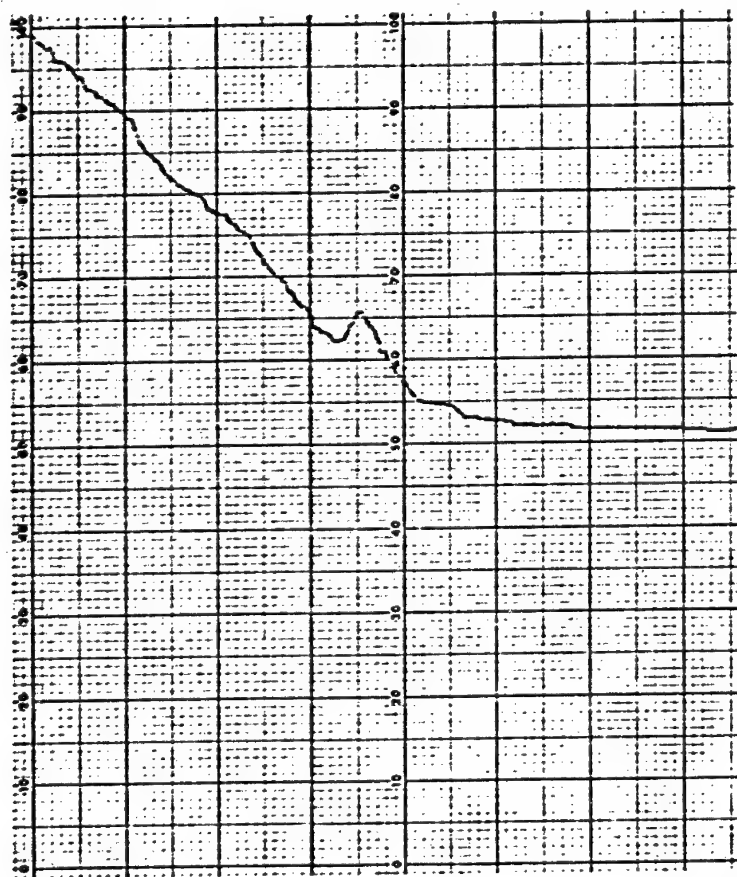


Figure 14. IR of Polysebacamide (4).



527°K  
Figure 15. DSC of Polysebacanide (4).

373°K

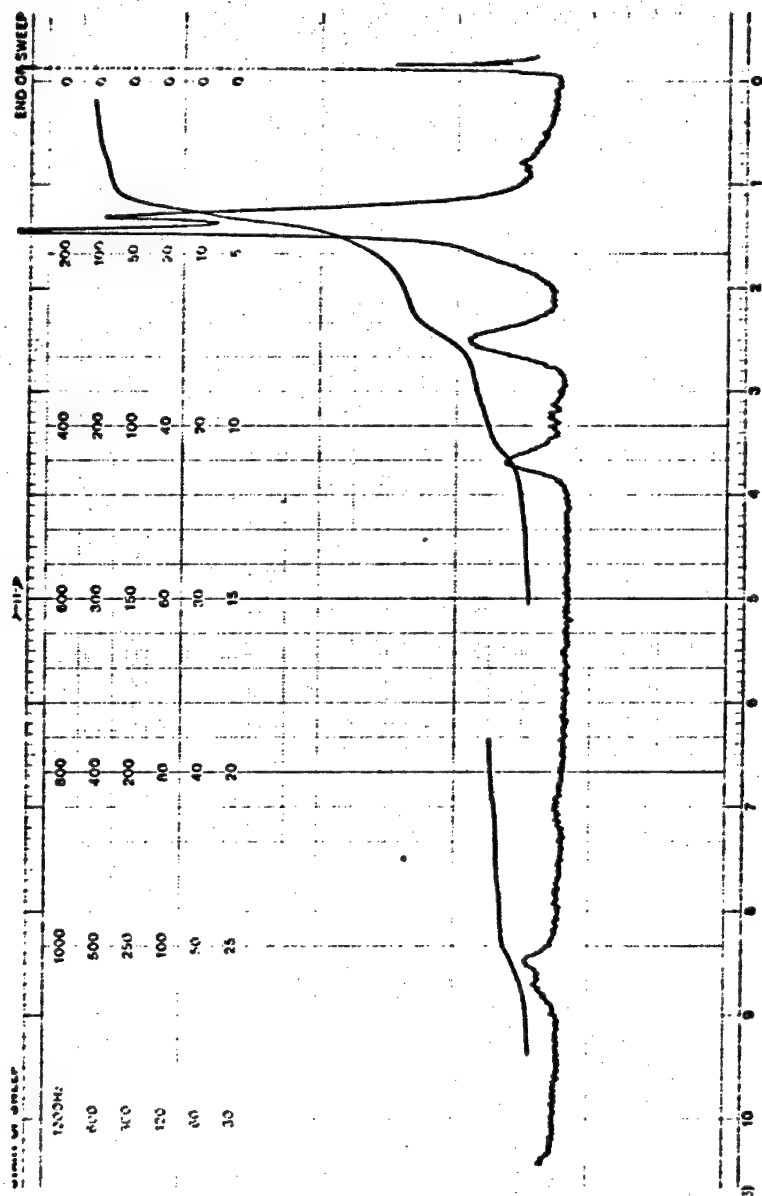
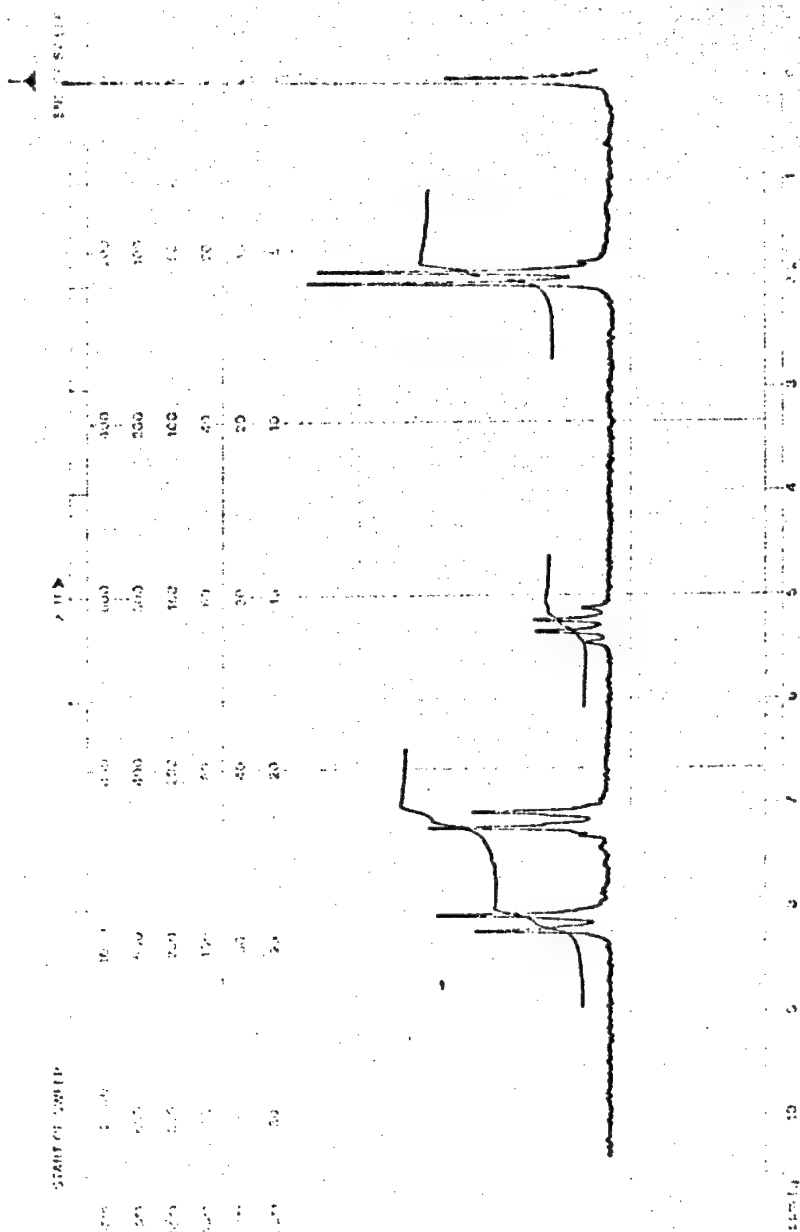


Figure 16. NMR of Polysebacamide (6).



Figure 17. NMR of 4,4'-Bis(chloroacetyl)diphenyl ether (15).



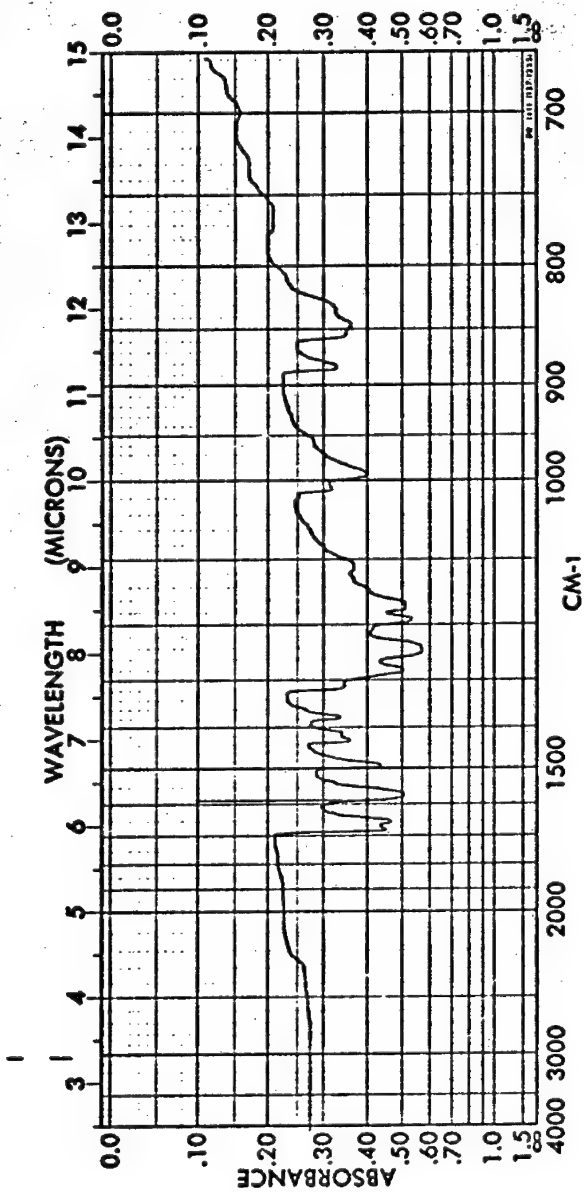


Figure 19. IR of 4,4'-Bis(bromoacetyl)diphenyl ether (16).

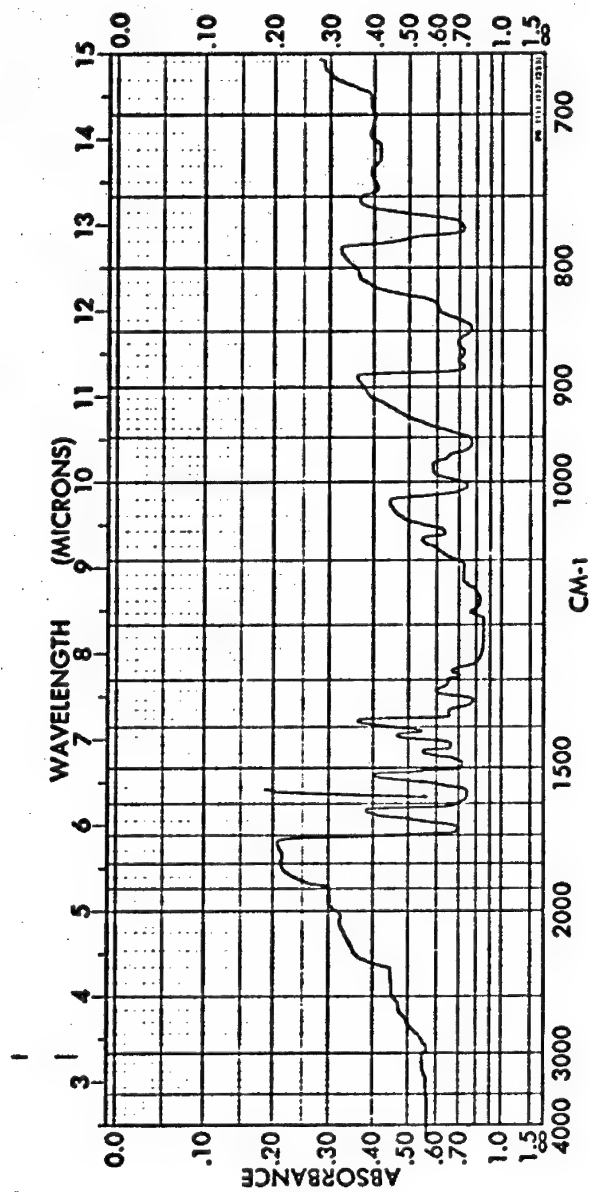
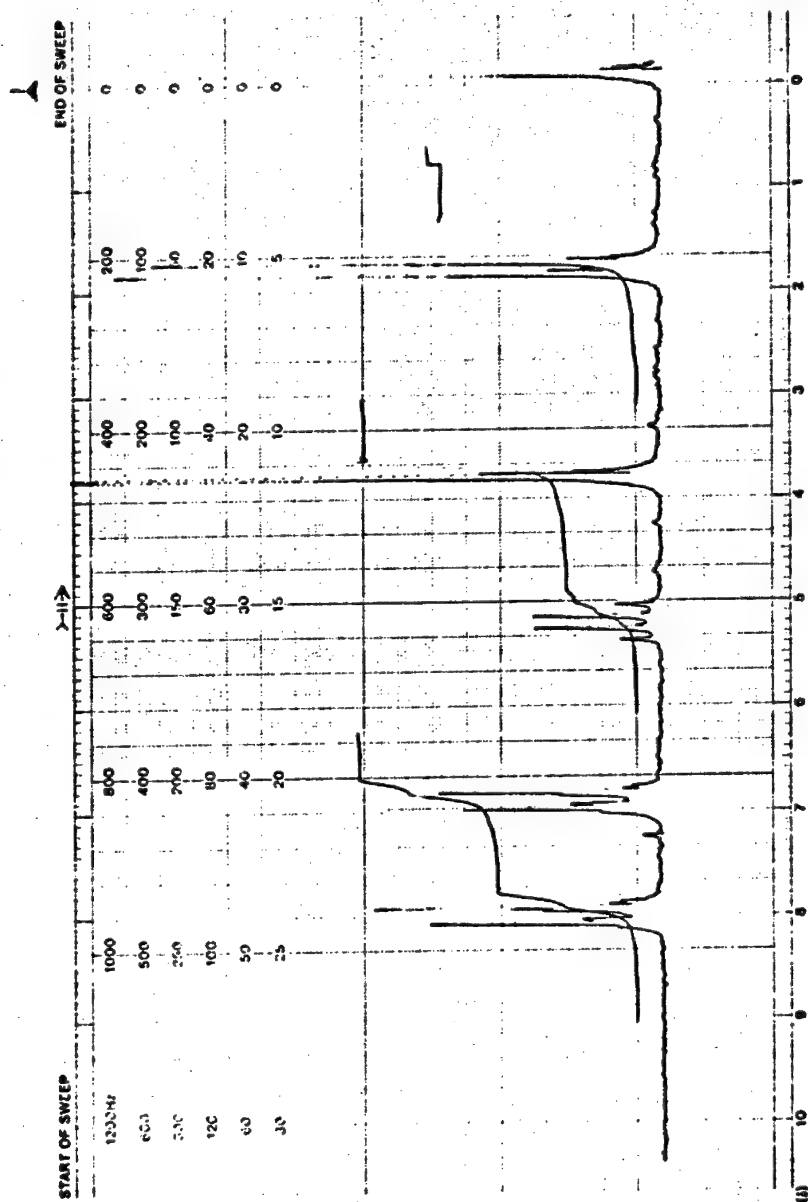


Figure 20. IR of 4,4'-Bis(2-chloropropionyl)diphenyl ether (18).

Figure 21. NMR of  $\alpha$ -bromo-p-methoxypropylphenone (39).

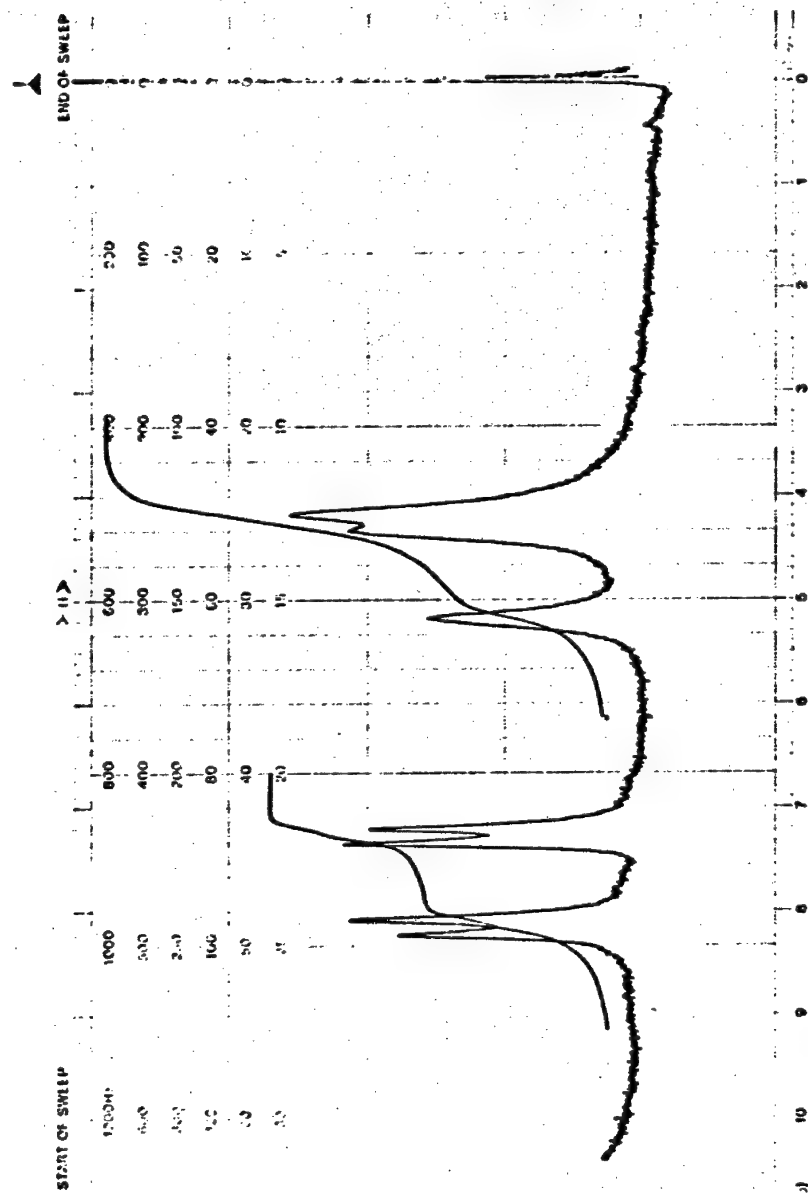


Figure 22. NMR of Polyamine (25).

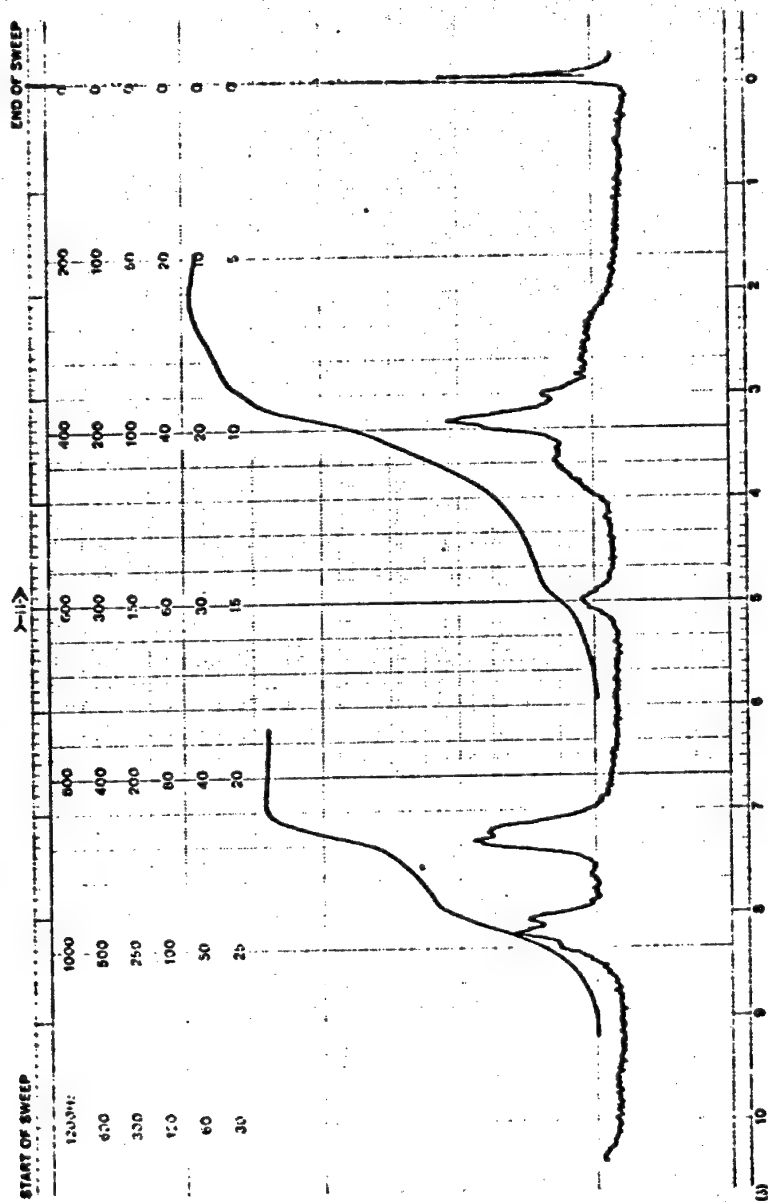


Figure 23. NMR of Polyamine (28).

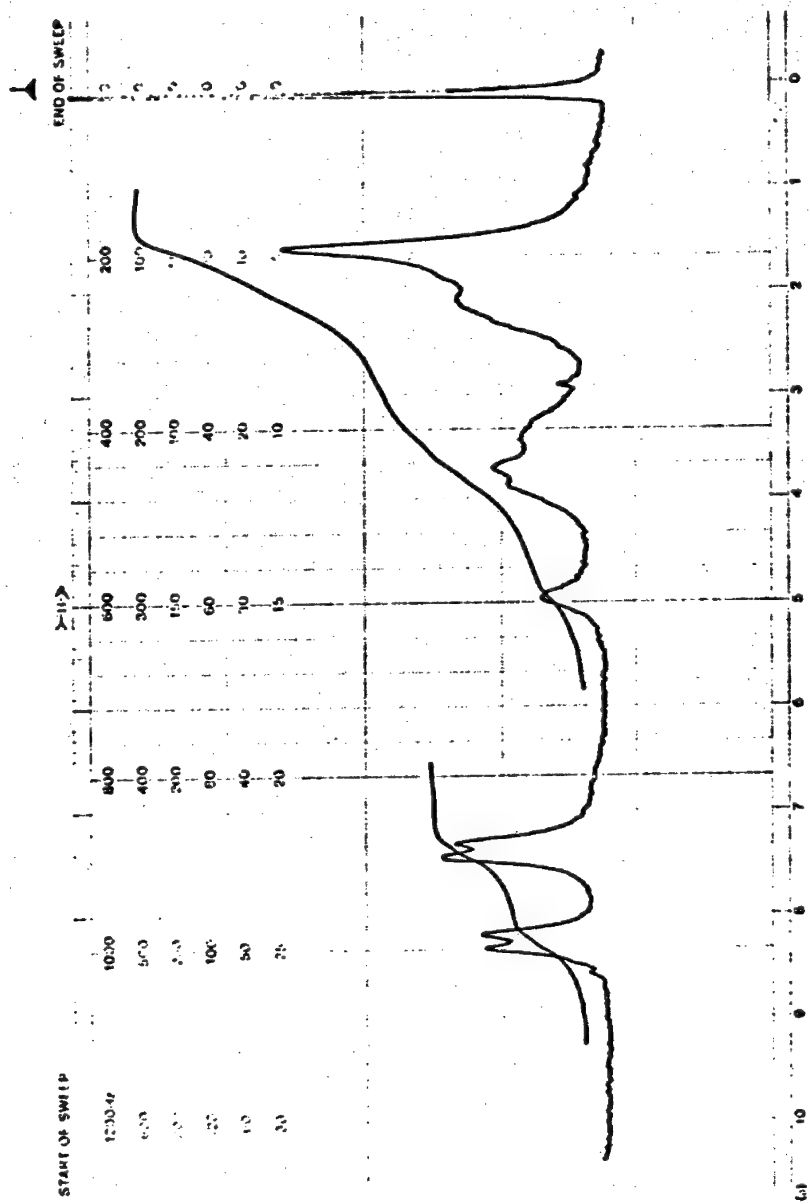


Figure 24. NMR of Polyamine (33).

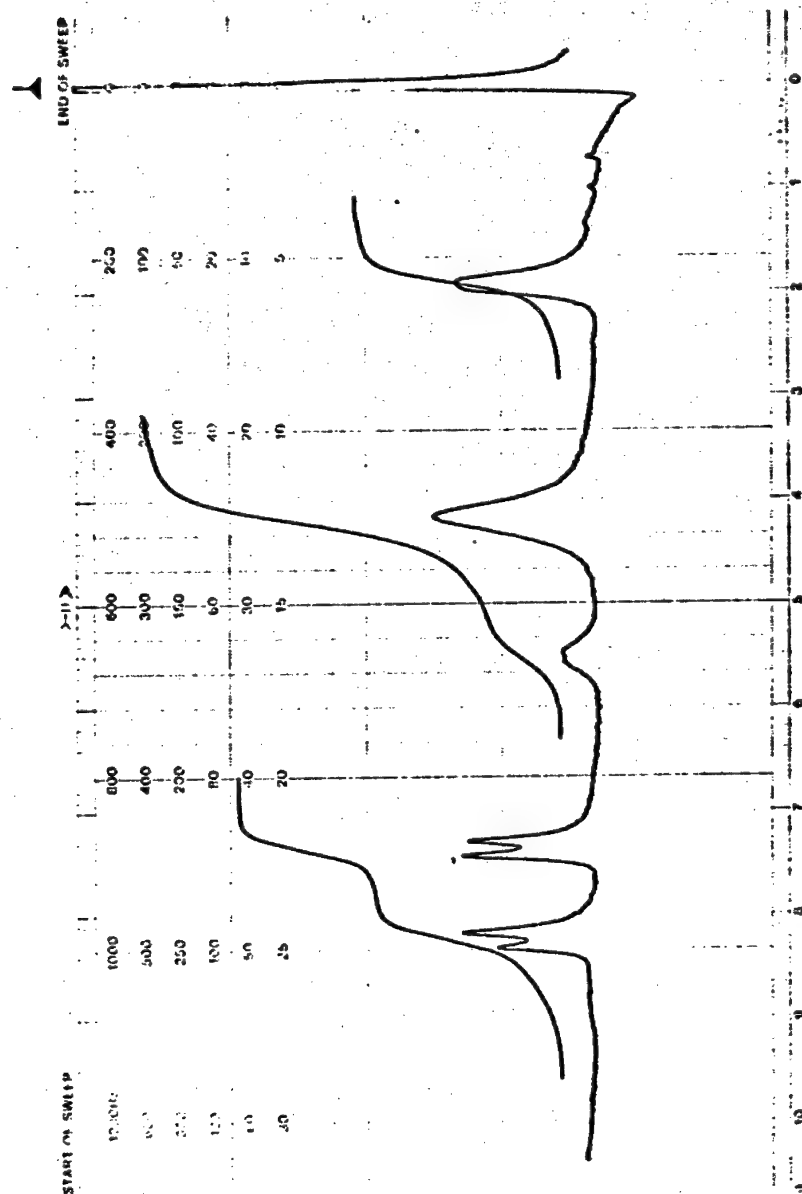


Figure 25. NMR of Polyaniline (34).

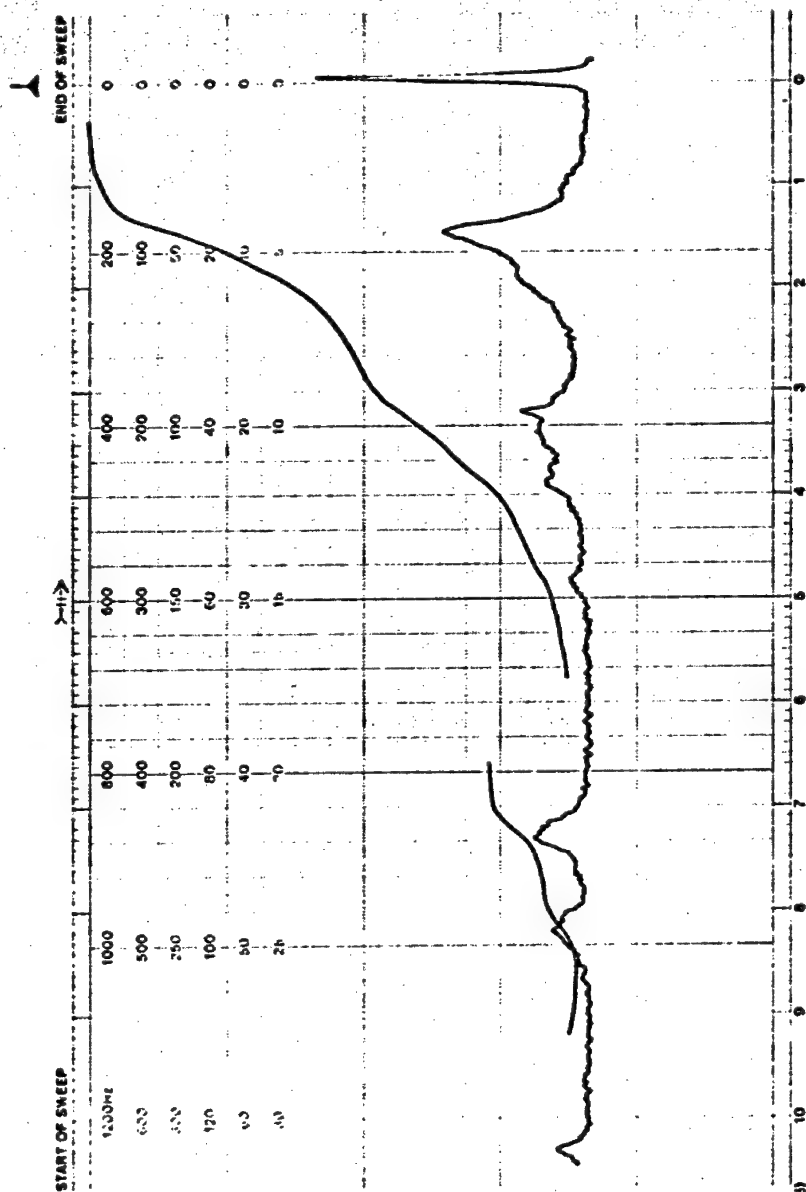


Figure 26. NMR of Extended Polyamine (36).

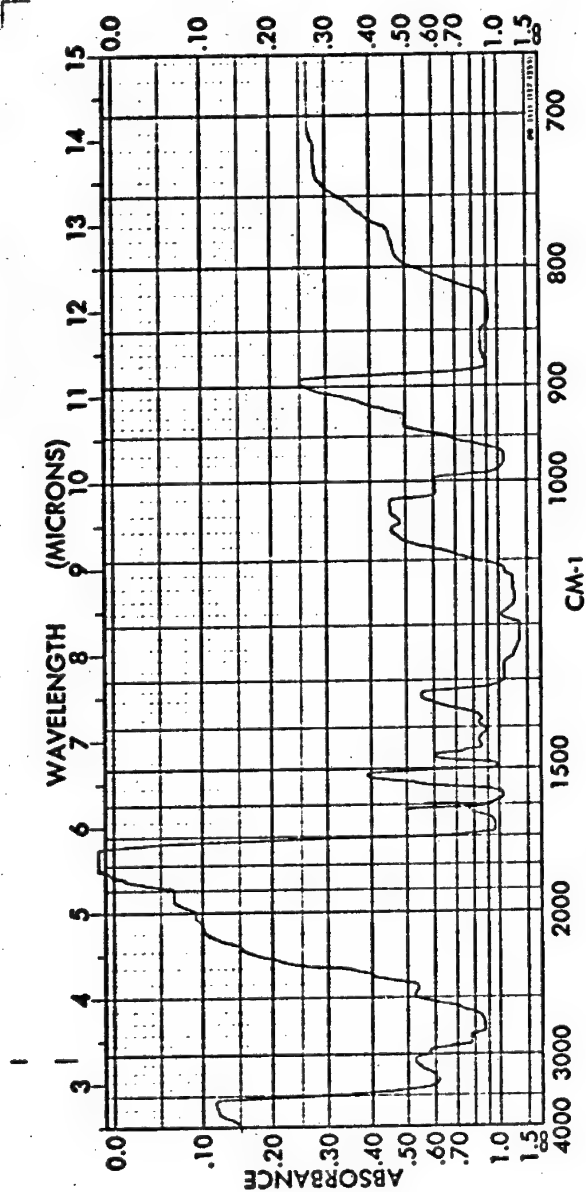


Figure 27. IR of Polyamine (20).

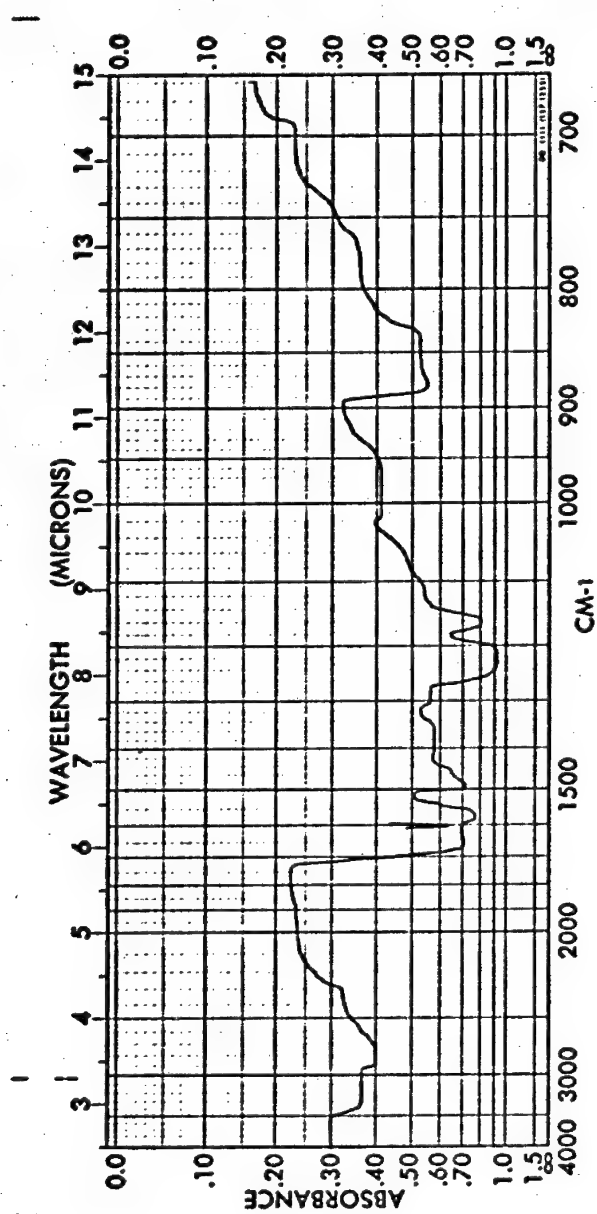


Figure 28. IR of Polyamine (29).

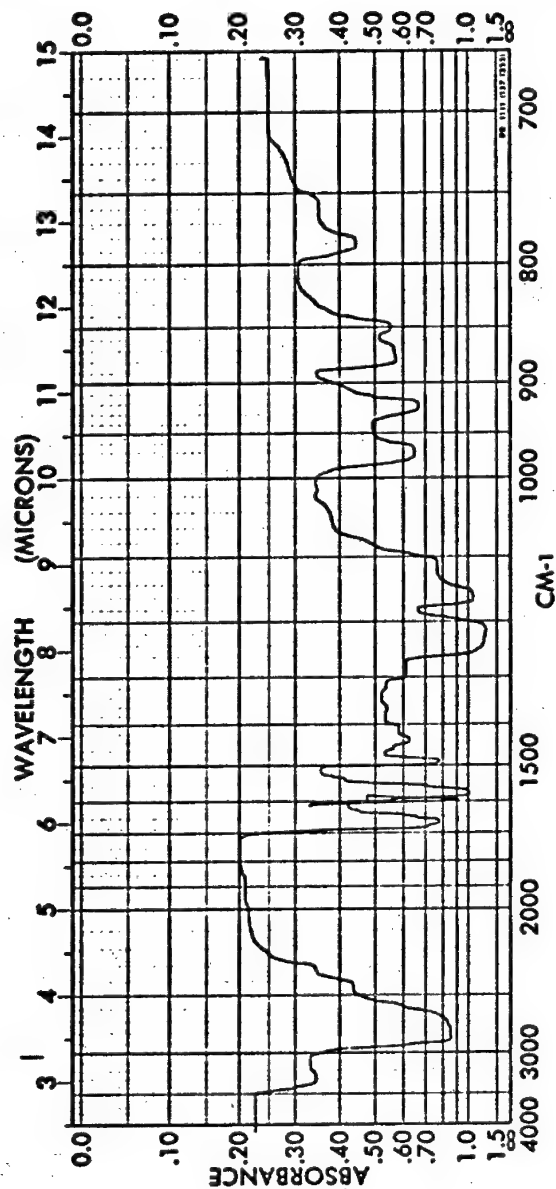


Figure 29. IR of Polyamine (35).

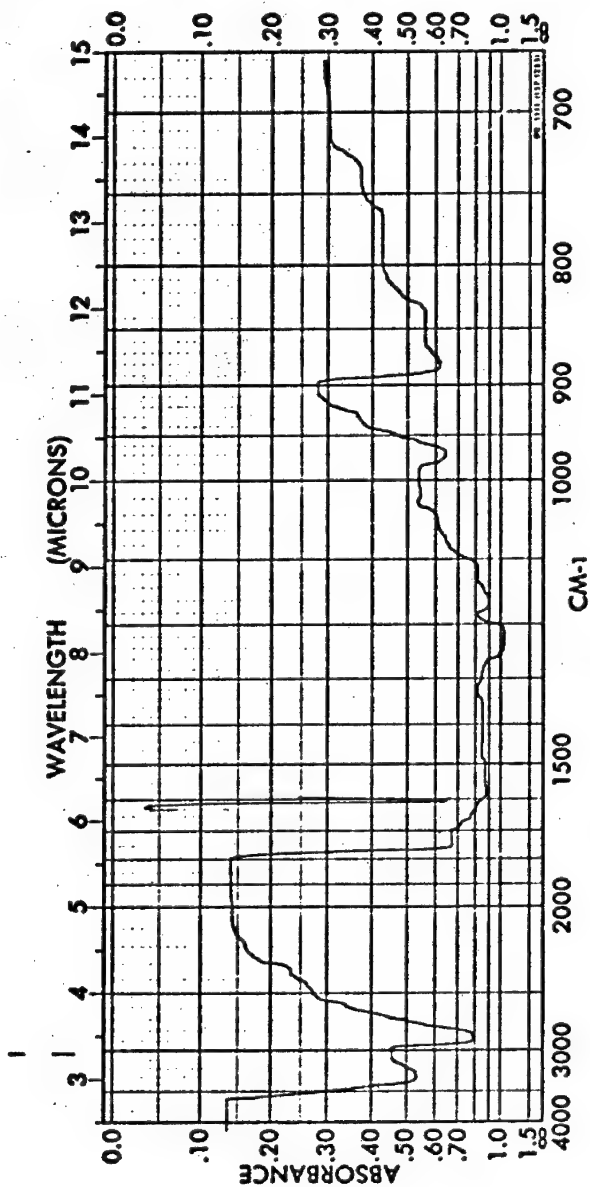


Figure 30. IR of Extended Polyamine (36).

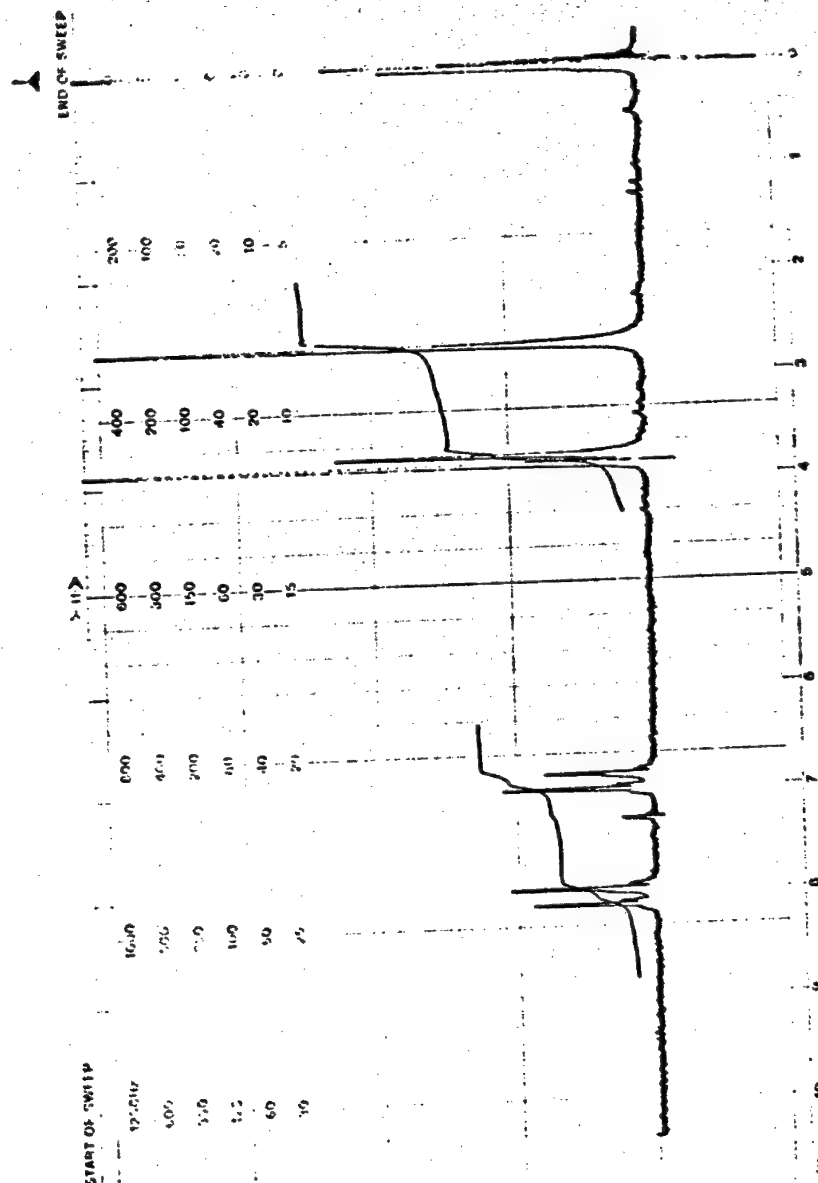


Figure 31. NMR of Model Compound (37).

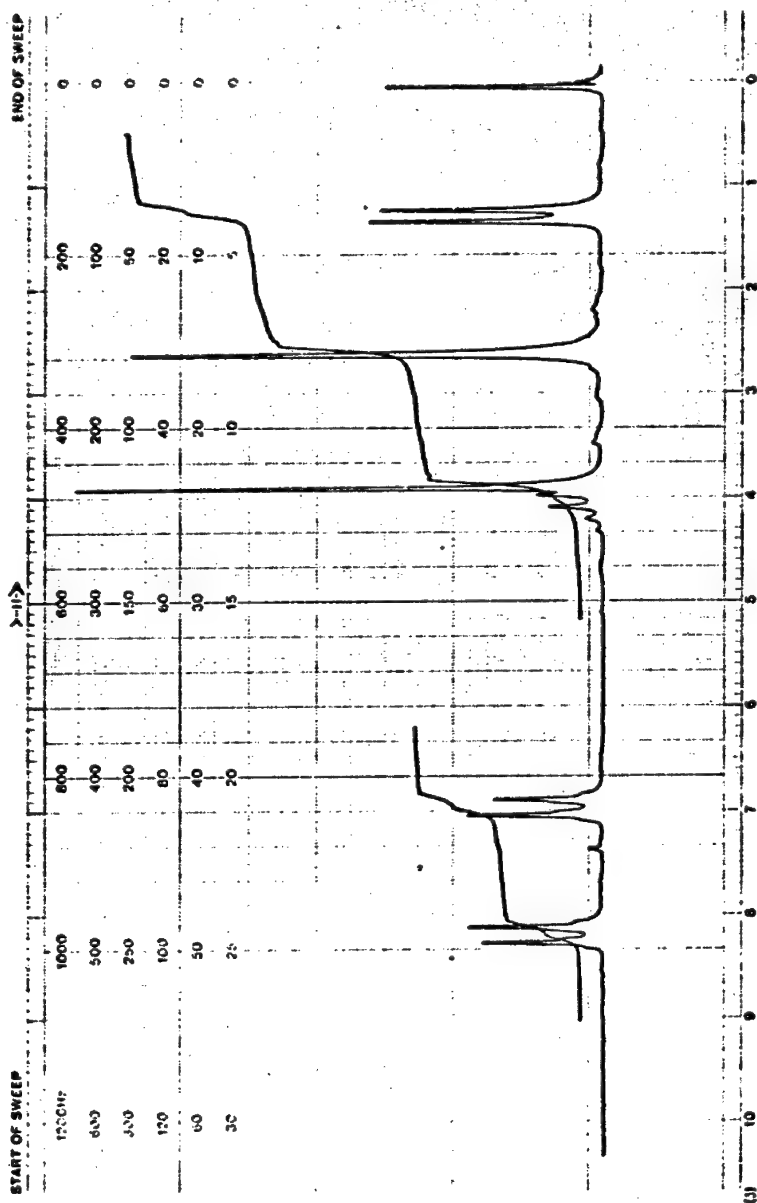


Figure 32. NMR of Model Compound (38).

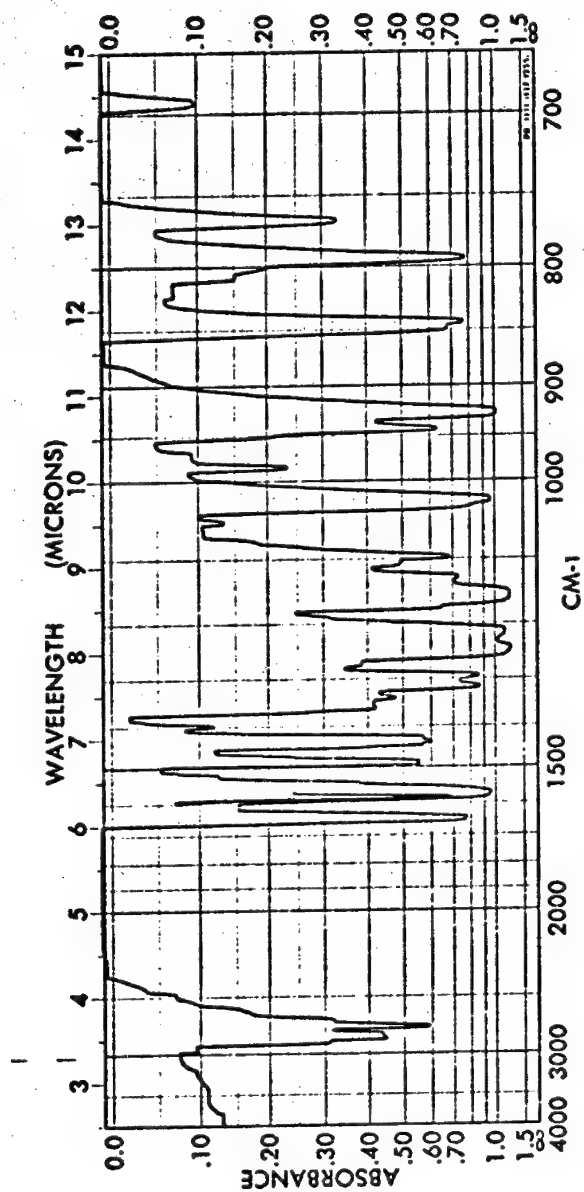
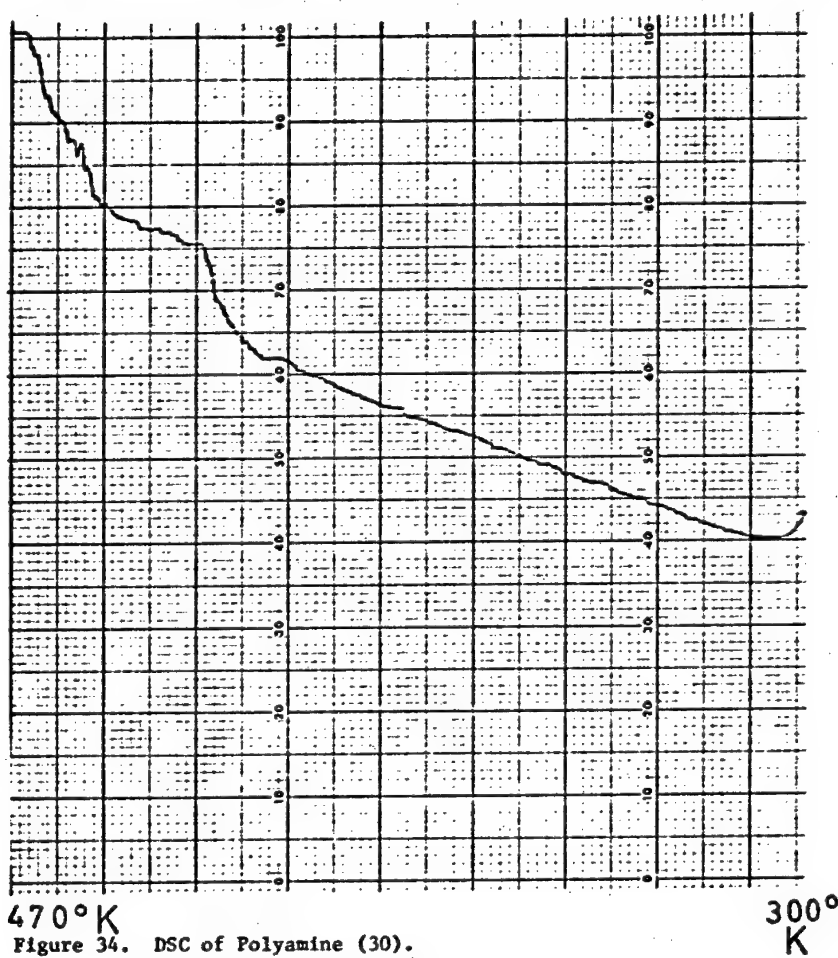


Figure 33. IR of Model Compound (38).



470°K

Figure 34. DSC of Polyamine (30).

300°K

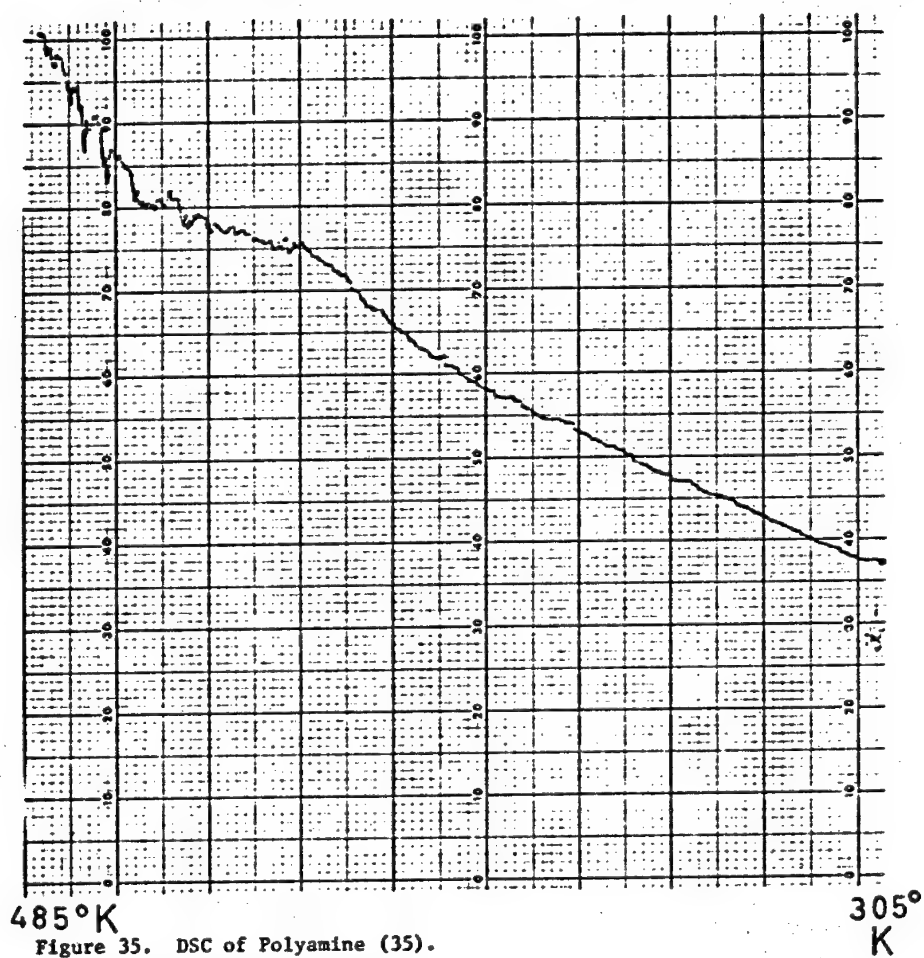


Figure 35. DSC of Polyamine (35).

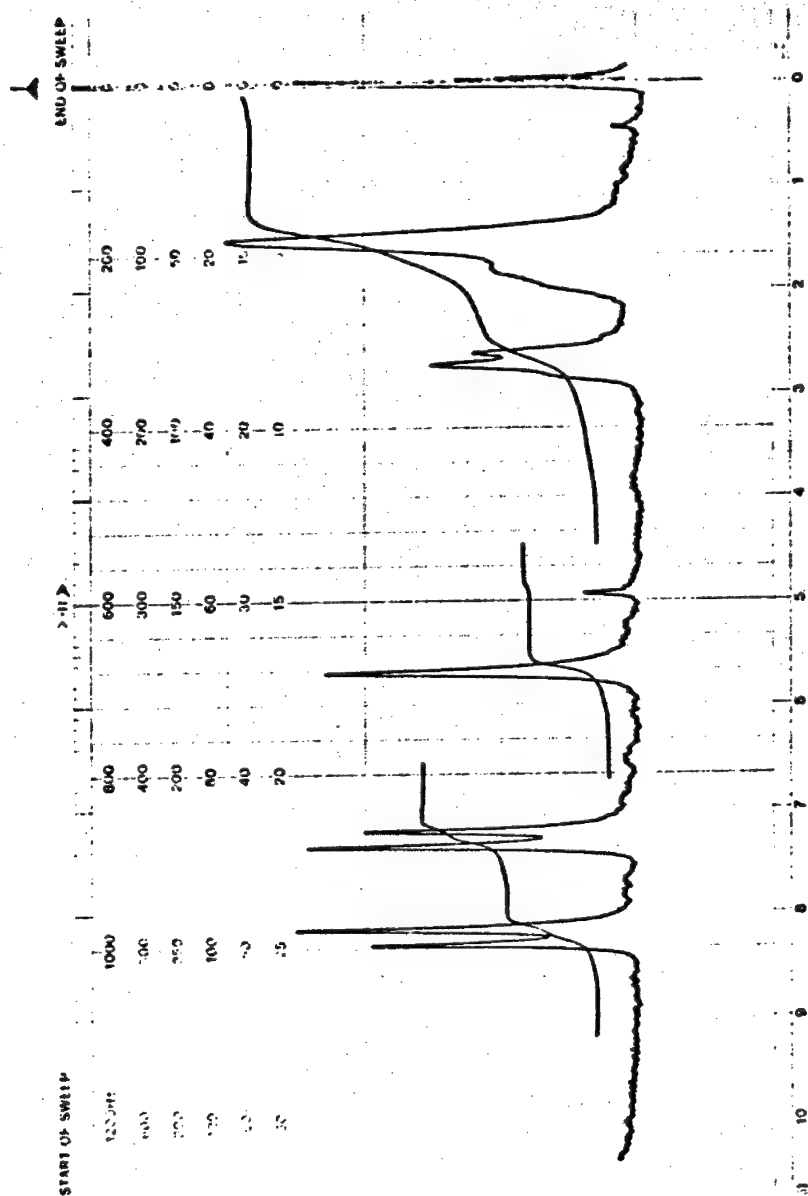


Figure 36. NMR of Polyester (43).



**Figure 37. NMR of Polyester (44).**

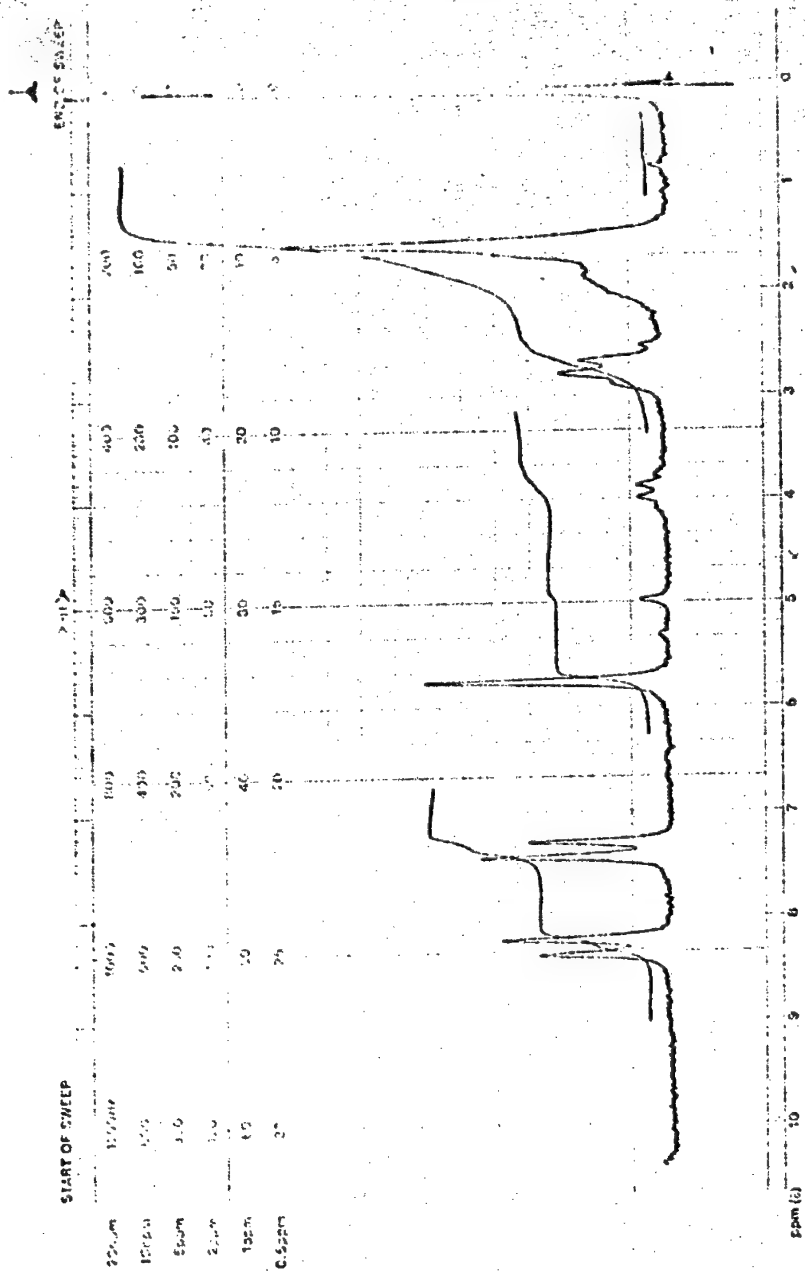


Figure 38. NMR of Polyester (48).

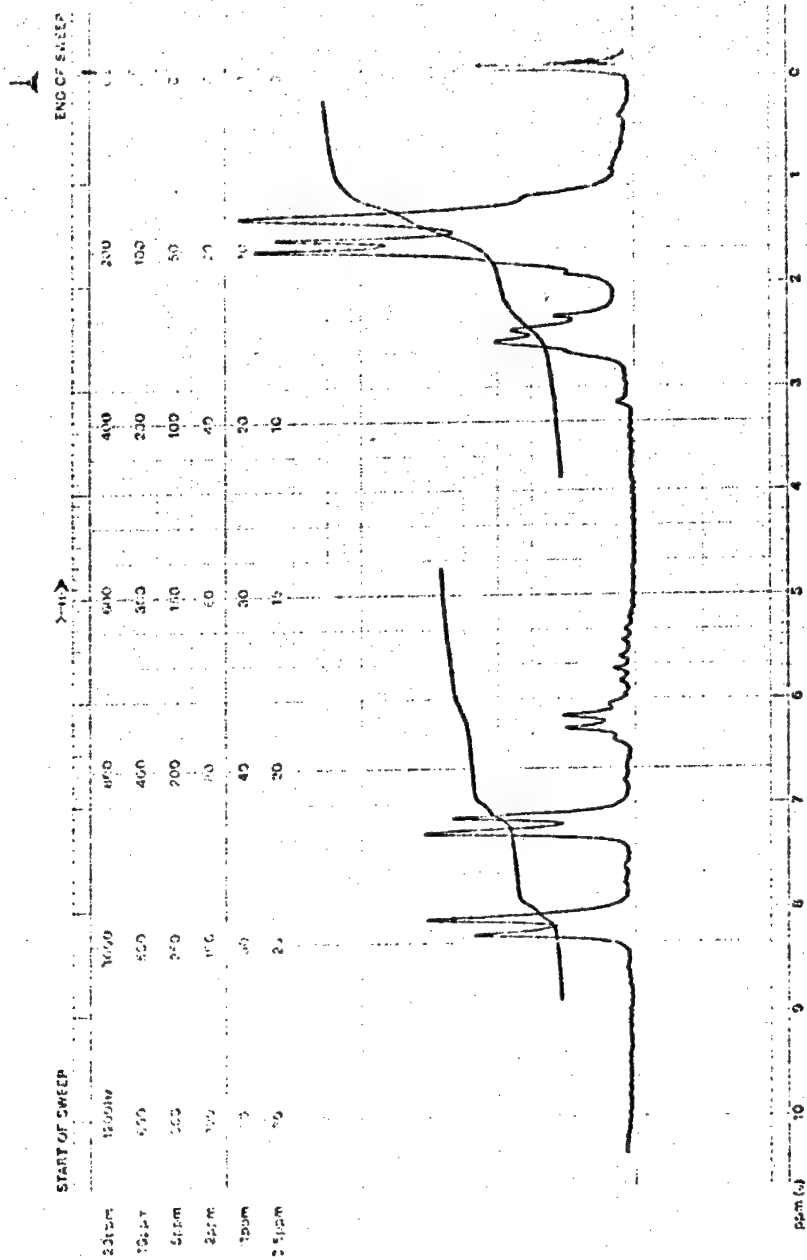


Figure 39. NMR of Polyester (50).

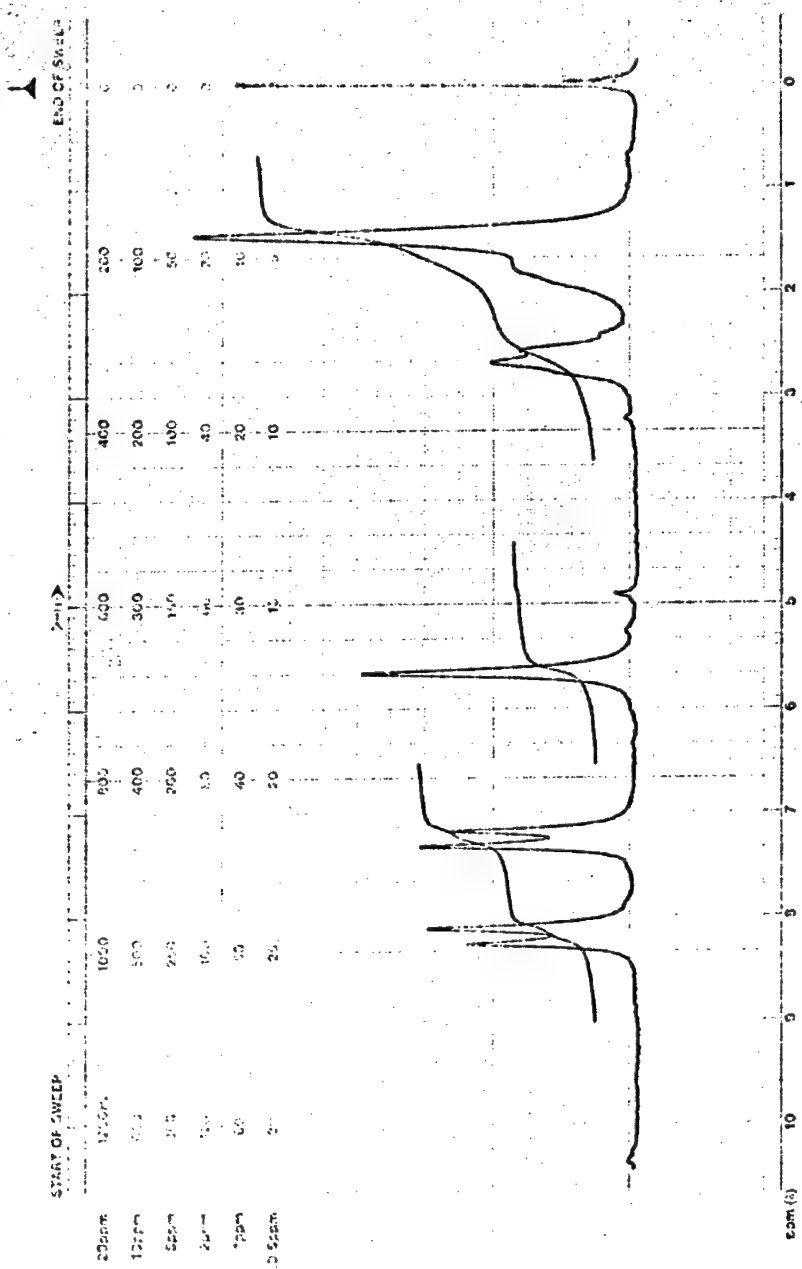


Figure 40. NMR of Polyester (52).

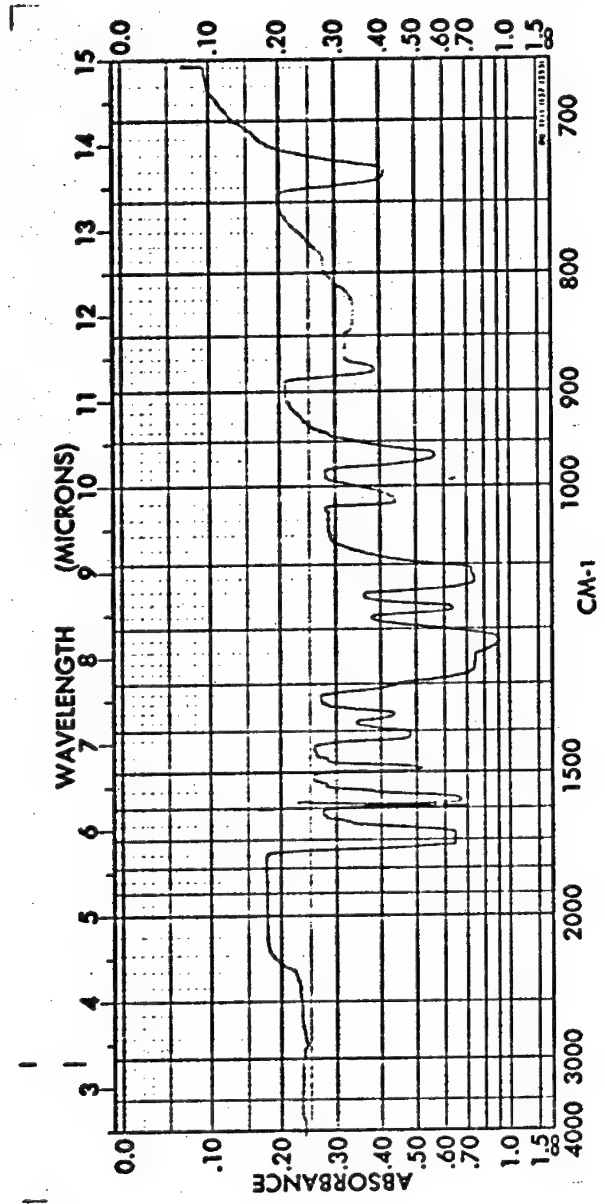


Figure 41. IR of Polyester (39).

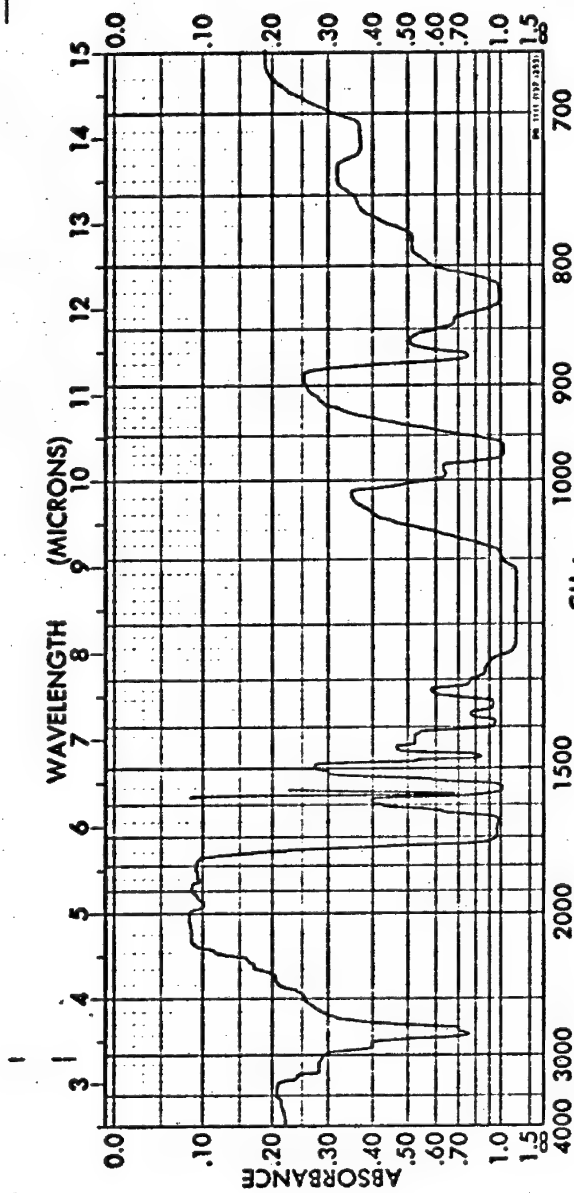


Figure 42. IR of Polyester. (45).

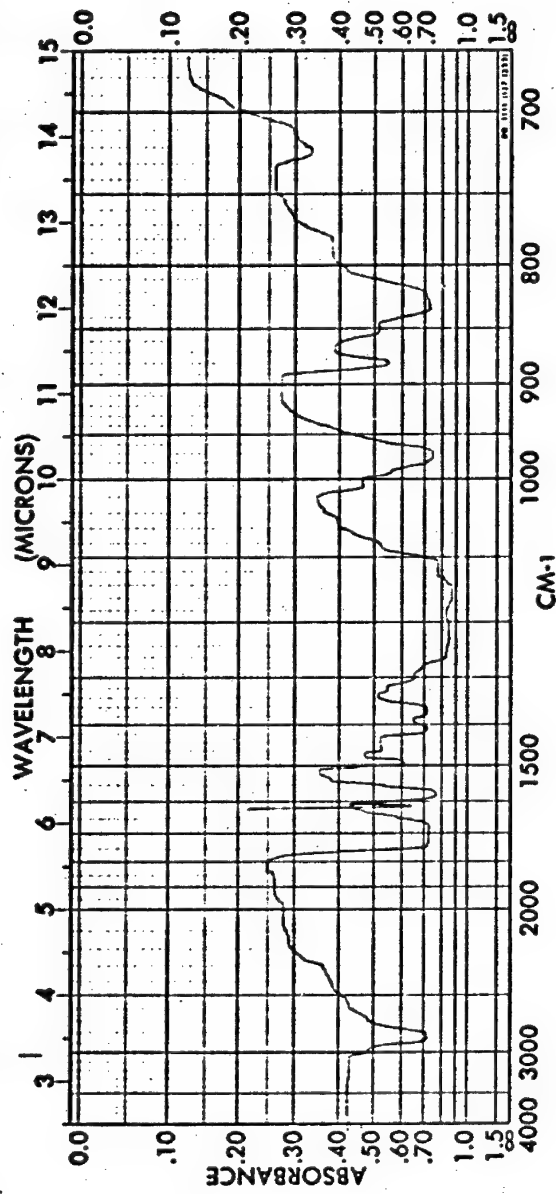


Figure 43. IR of Polyester (47).

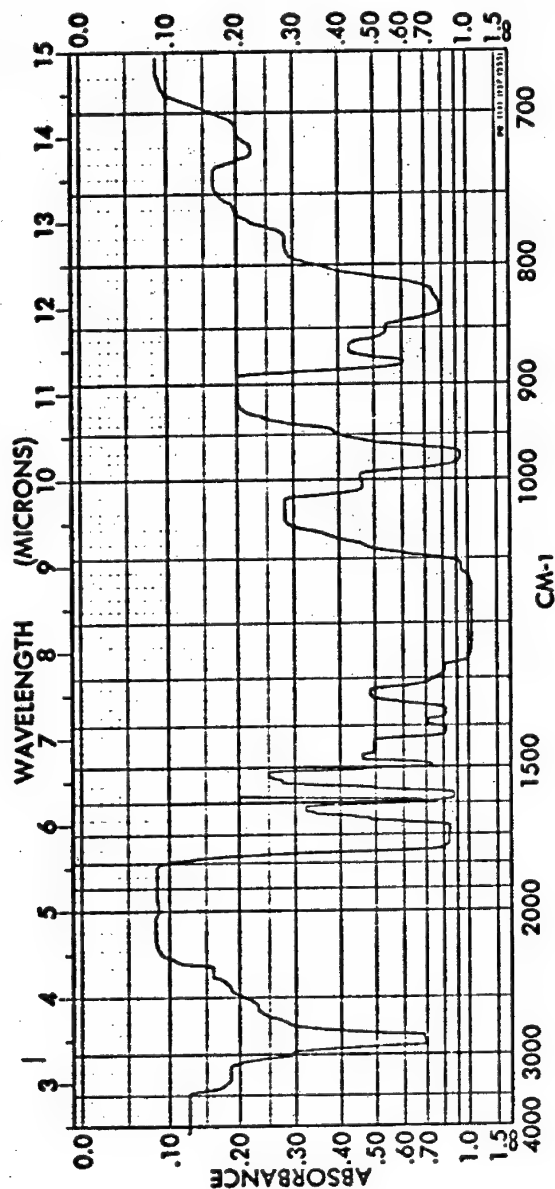


Figure 44. IR of Polyester (48).

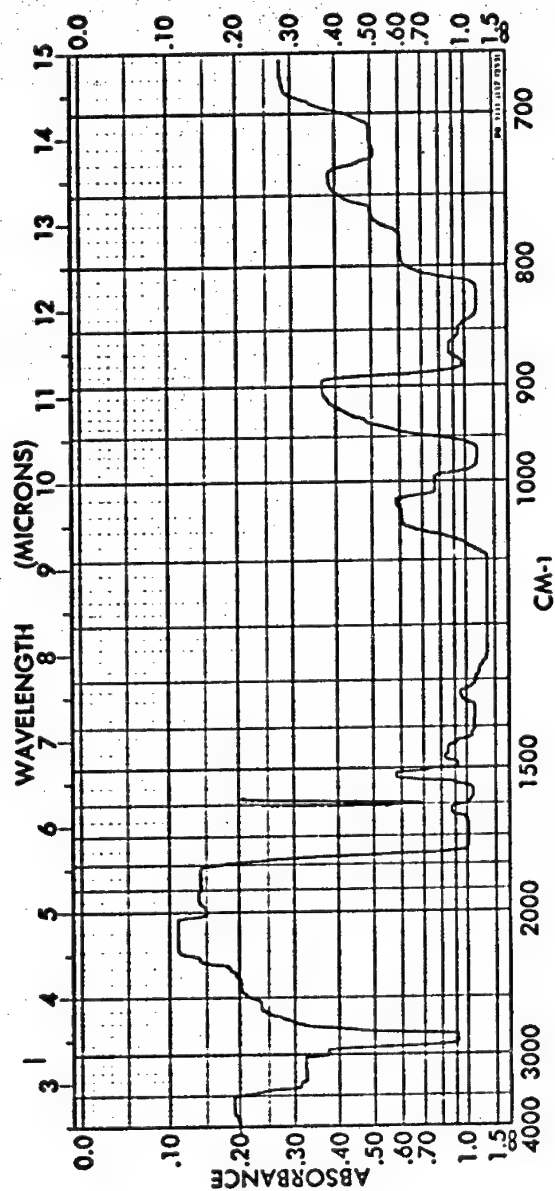
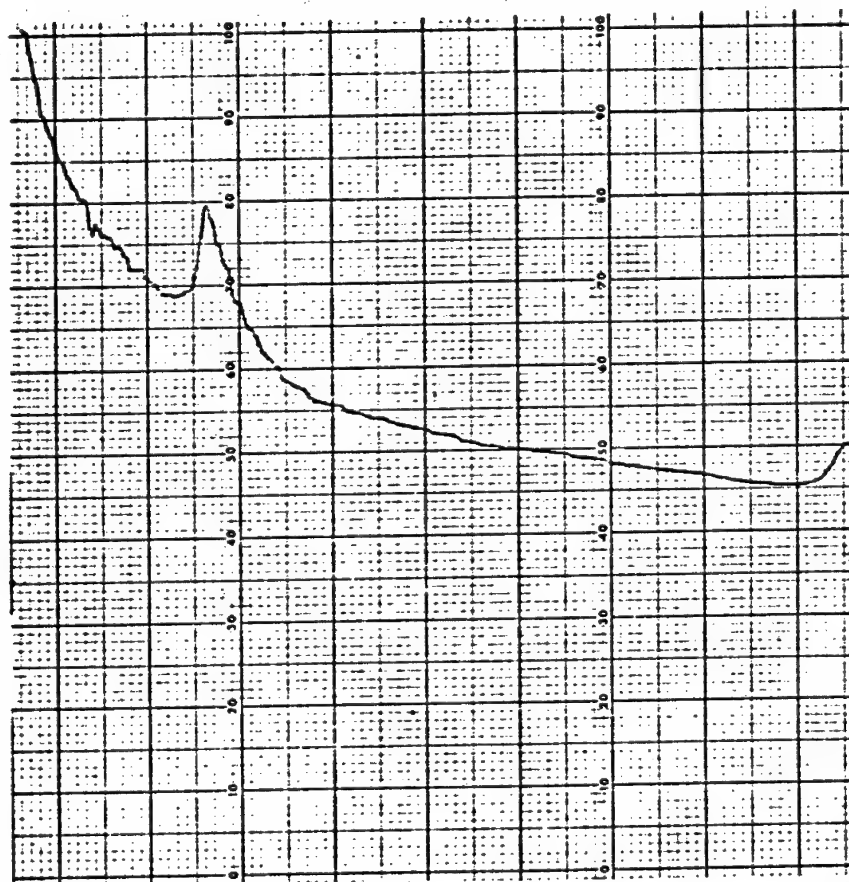


Figure 45. IR of Polyester (52).



480°K  
Figure 46. DSC of Polyester (46).

300°  
K

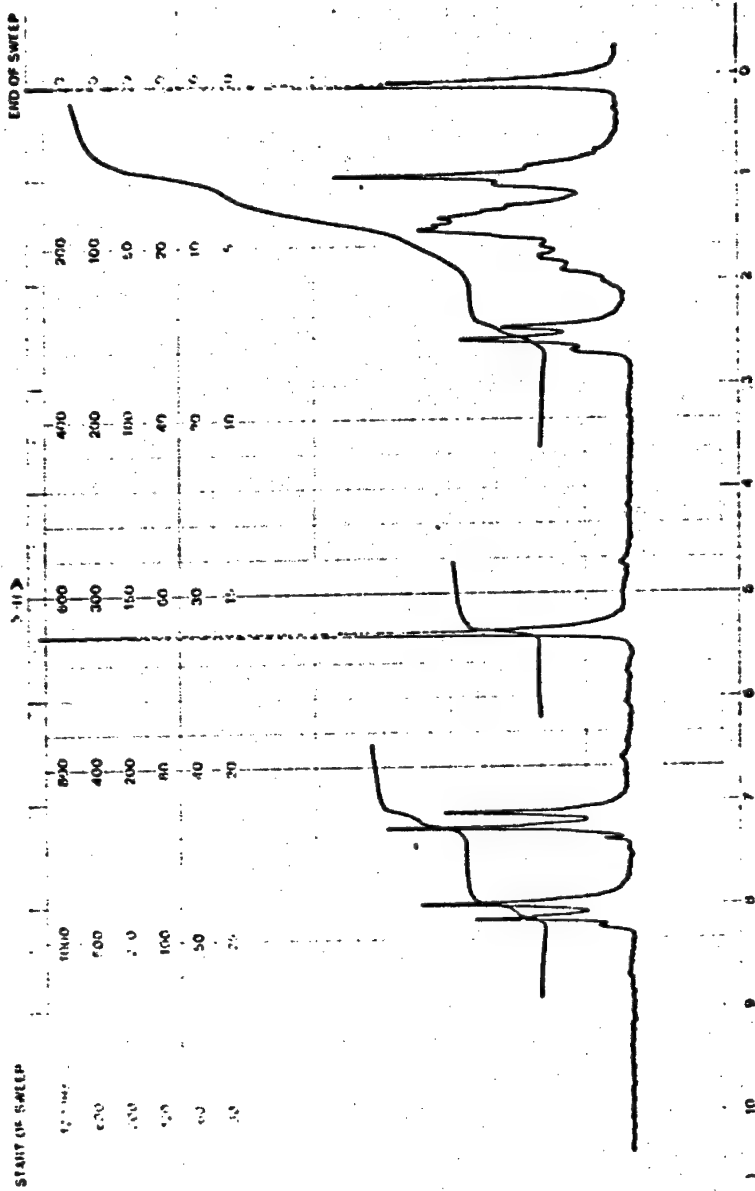


Figure 47. NMR of Model Compound (54).

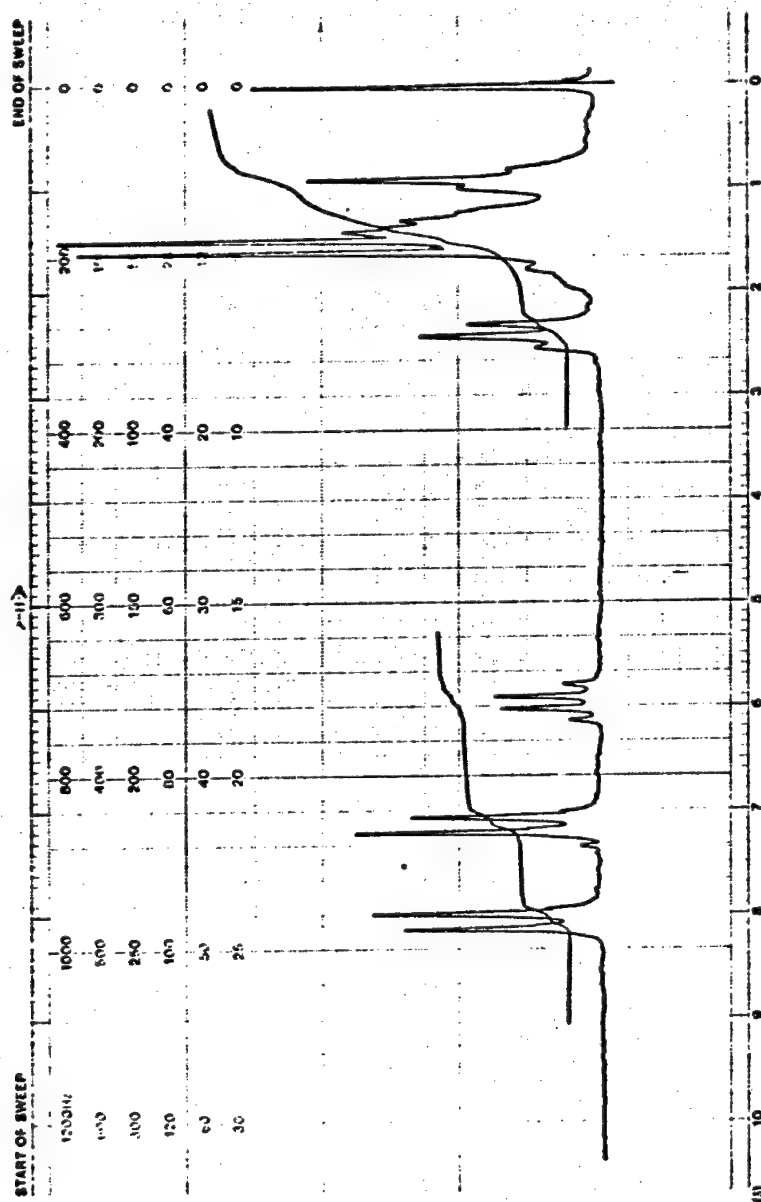


Figure 48. NMR of Model Compound (55).

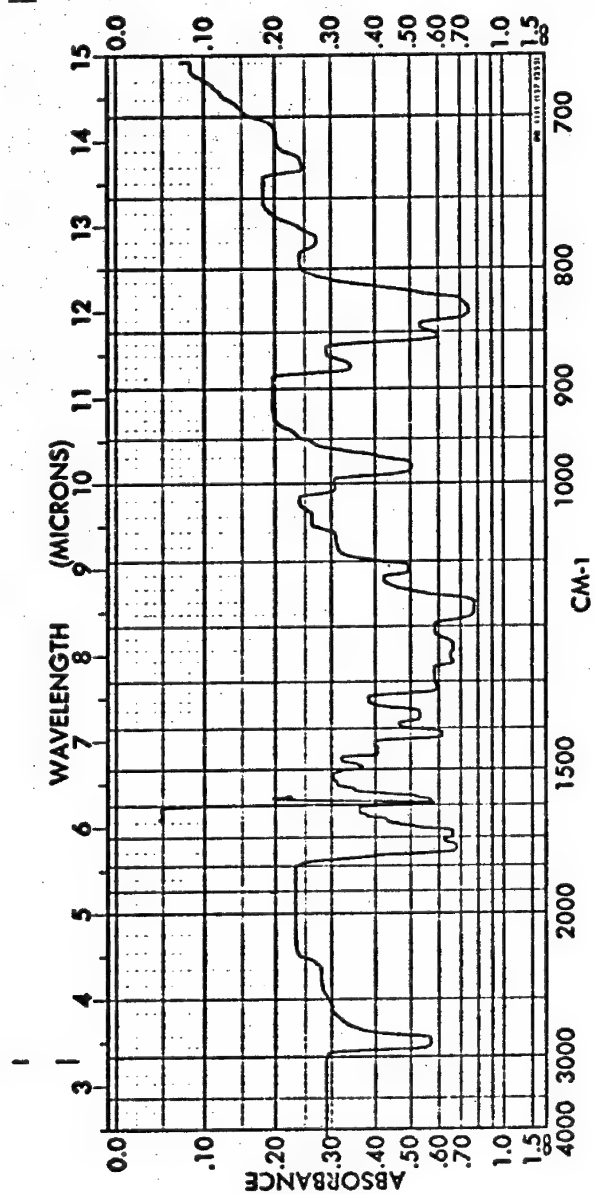


Figure 49. IR of Model Compound (54).

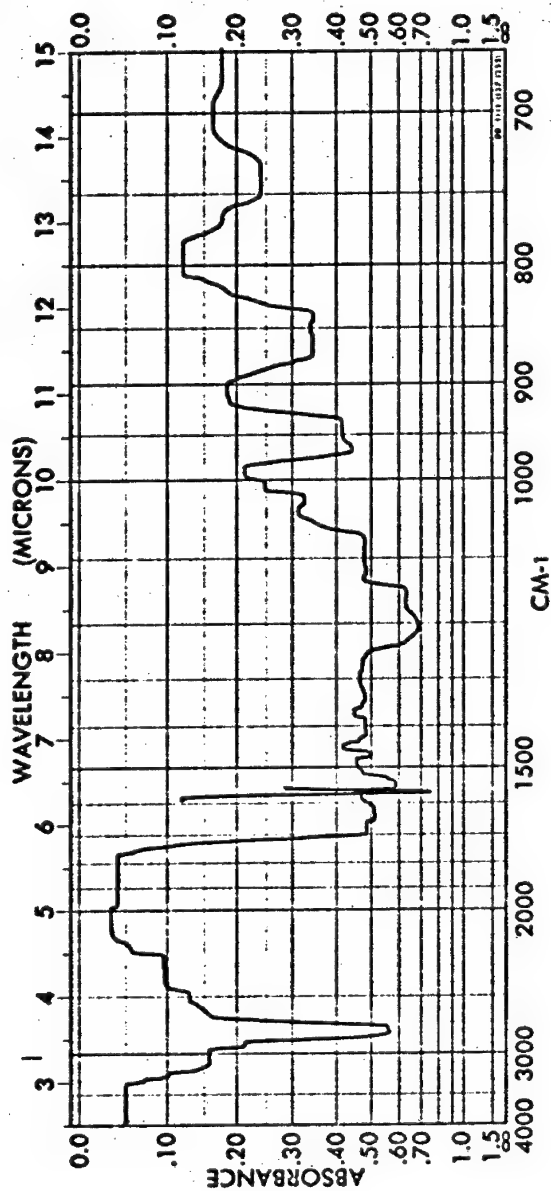


Figure 50. IR of Model Compound (55).

## VI. SUMMARY

Biodegradable polysebacamides have been subjected to ultraviolet irradiation. Unsubstituted poly(ethylene sebacamide) and methyl substituted polysebacamides were photodegradable. Poly(piperazine sebacamide) and phenyl and hydroxy substituted polysebacamides were crosslinked by light, due to the formation of stable free radicals. The polysebacamides were more degradable by *Aspergillus niger* after irradiation.

Polyamines synthesized from 4,4'-bis(chloroacetyl)diphenyl ether, and its bromoacetyl and bromopropionyl analogs were found to be photodegradable. The greatest degradation occurred in polymers from the bis(propionyl)diphenyl ether. These polymers were not utilized by microorganisms, either before or after photolysis.

Polyesters prepared from the bis(chloroacetyl)diphenyl ether and diacids of eight or more carbon atoms were biodegraded by *Aspergillus niger*, but were crosslinked by light. There was no difference in the growth of *niger* on photolyzed and unphotolyzed samples. This series of polyesters contains aromatic rings at regular intervals along the polymer backbone and is still biodegradable.

## VII. BIBLIOGRAPHY

1. P. Engler and S. H. Carr. 1973. J. Polym. Sci. Polym. Phys. Ed. 11, 313.
2. S. L. Kim, V. Stannett and R. D. Gilbert. 1973. J. Polym. Sci. Polym. Letters 11, 731.
3. G. J. L. Griffin. 1973. German 2,333,440.
4. R. J. Dennenberg, R. J. Bothast and T. P. Abbott. 1978. J. Appl. Polym. Sci. 22, 459.
5. J. E. Potts, R. A. Clendinning, W. B. Ackart and W. D. Niegisch. 1973. Polymers and Ecological Problems, J. Guillet, ed., Plenum Press, N.Y., pp. 61-79.
6. W. Bailey. 1976. Proc. 3rd Int. Biodeg. Symp., J. M. Sharpley and A. M. Kaplan, eds., Appl. Sci. Publishers, London, pp. 765-773.
7. R. G. Sinclair. 1973. Environ. Sci. Tech. 7, 955.
8. R. L. Kronenthal. 1975. Polymers in Medicine and Surgery, R. L. Kronenthal, Z. Oser and E. Martin, eds., Plenum Press, N.Y., pp. 119-137.
9. H. F. Weyn. 1973. French 2,178,461.
10. S. G. Gilbert, K. J. Giacin, T. Van Gordon, A. Vahidi and J. R. Giacin. 1974. Amer. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap, 34, 462.
11. S. L. Kim. 1974. Diss. Abstr. Int. B 35, 1121.
12. J. A. Pavlisko. 1978. Ph.D. thesis, University of Connecticut.
13. K. W. Leong. 1977. Ph.D. thesis, University of Connecticut.
14. H. Hatakeyama. 1977. Japan Kokai 77 58,783.
15. R. A. Clendinning, J. E. Potts and S. W. Cornell. 1975. U.S. 3,921,333.
16. R. A. Clendinning, J. E. Potts and W. D. Niegisch. 1976. U.S. 3,932,319.
17. ASTM Standards D1924-70.

18. I. Tabushi, H. Yamada, O. Arita, S. Matsuo and J. Furukawa. 1976. Japan-USSR Polym. Symp. [Proc.] 2nd, Soc. Polym. Sci., Tokyo, Japan, pp. 365-72. (CA85: 63767f).
19. M. Bitritto-Vallini. 1976. Ph.D. thesis, University of Connecticut.
20. B. S. Hartley and D. M. Shotton. 1971. The Enzymes, Vol. III, Hydrolysis: Peptide Bonds, P. D. Boyer, ed., Academic Press, N.Y. pp. 323-339.
21. a) P. I. Plooard and J. E. Guillet. 1972. Macromolecules 5, 405; b) B. Ranby and J. F. Rabek. 1975. Photodegradation, Photo-oxidation and Photostabilization of Polymers, John Wiley and Sons, N.Y., pp. 48-49; c) K. Sugita, T. Kilp and J. E. Guillet. 1976. J. Polym. Sci.: Polym. Chem. Ed. 14, 1901; d) P. J. Wagner. 1971. Accounts of Chemical Research 4, 168.
22. a) G. H. Hartley and J. E. Guillet. 1968. Macromolecules 1, 165; b) M. Heskins and J. E. Guillet. 1970. Macromolecules 3, 224.
23. Y. Amerik and J. E. Guillet. 1971. Macromolecules 4, 375.
24. Y. Shimura. 1978. J. Appl. Polym. Sci. 22, 1491.
25. E. Dan and J. E. Guillet. 1973. Macromolecules 6, 230.
26. a) J. Lukac, M. Moravcik and P. Hrdlovic. 1974. J. Polym. Sci.: Polym. Chem. 12, 1913; b) I. Lukac, J. Pilka, M. Kulickova and P. Hrdlovic. 1977. J. Polym. Sci.: Polym. Chem. 15, 1645.
27. L. R. Spencer, M. Heskins and J. E. Guillet. 1976. Proc. 3rd Int. Biodeg. Symp., J. M. Sharpley and A. M. Kaplan, eds., Appl. Sci. Publishers, London, pp. 753-763.
28. J. D. Cooney, D. M. Wiles. 1974. Soc. Plast. Eng. Tech. Pap. 20, 420.
29. C. E. Swanholm and R. G. Caldwell. 1975. Fr. Demande 2,234,337.
30. N. B. Nykvist. 1974. Plast. Polym. 42 (161), 195. (CA83: 115260r).
31. M. Hamoud, M. Vert and E. Selegny. 1972. J. Polym. Sci. B. 10, 361.
32. R. G. Beaman, P. W. Morgan, C. R. Koller, E. L. Wittbecker and E. E. Magat. 1959. J. Polym. Sci. 40, 329.
33. S. J. Huang and M. Roby, unpublished results.
34. J. G. Calvert and J. N. Pitts. 1966. Photochemistry, John Wiley and Sons, Inc., N.Y., p. 460.

35. V. V. Korshak and S. R. Rafikov. 1944. J. Gen. Chem. (USSR) 14, 974. (CA39: 4592<sup>7</sup>).
36. B. Fukuda, S. Namba and H. Nabeshima. 1965. Nippon Secchaku Kyokai Shi 1, 24. (CA67: 74090j).
37. P. W. Morgan and S. L. Kwolek. 1964. J. Polym. Sci. A-2, 181.
38. A. Padwa and D. Eastman. 1969. J. Amer. Chem. Soc. 91, 462.
39. D. Bansleben. 1975. M.S. Thesis, University of Connecticut.
40. R. G. Neville and J. W. Mahoney. 1967. J. Appl. Polym. Sci. 11, 2029.
41. A. DiChamp, J. P. Tortai and E. Marechal. 1972. Bull. Soc. Chim. Fr., 3234.
42. J. A. Hyatt. 1972. J. Org. Chem. 37, 1254.
43. J. C. Sheehan and K. Umezawa. 1973. J. Org. Chem. 38, 3771.
44. D. P. N. Satchell and R. S. Satchell. 1975. Chem. Soc. Rev. 4, 231.
45. E. A. Collins, J. Bares and F. W. Billmeyer, Jr. 1973. Experiments in Polymer Science, Wiley-Interscience, N.Y., pp. 362-67.
46. A. J. Gordon and R. A. Ford. 1972. The Chemist's Companion, John Wiley and Sons, Inc., N.Y., pp. 429-436.
47. E. A. Collins, J. Bares and F. W. Billmeyer, pp. 330-333.
48. D. Braun, H. Cherdron and W. Kern. 1972. Techniques of Polymer Synthesis and Characterization, John Wiley and Sons, Inc., N.Y., pp. 218-219.
49. O. von Schickh. 1929. U.S. 1,717,424.
50. H. Saikachi and H. Muto. 1971. Chem. Pharm. Bull. 19, 2262.
51. A. V. Dombrovskii, M. I. Shevchuk and V. P. Kravets. 1962. Zh. Obshch. Khim 32, 2278. (CA58: 7857q).